# Whispering Across the Hydrogen Bond: Asymmetric, Sign-Inverted Electronic Communication in β-Diketones

## A Hammett Study of Intramolecular Hydrogen Bond Strength

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**Abstract: The strength of the intramolecular hydrogen bond (IHB) in β-diketones is a critical determinant of their chemical behaviour and biological activity. Despite extensive Hammett studies on simple β-diketones, a quantitative linear free-energy relationship (LFER) analysis of asymmetrically multi-substituted dibenzoylmethane (DBM) derivatives – where both aryl rings bear substituents with differing electronic characters – remains unexplored. Twelve asymmetrically substituted DBM derivatives were synthesised via Claisen condensation. One aryl ring (Ring A) maintained a constant dimethoxy or trimethoxy pattern while the other (Ring B) was varied with electron-donating to strongly electron-withdrawing substituents. Compounds were characterised by $^1H$ and $^{13}C$ NMR spectroscopy, and chemical shifts were correlated with Hammett substituent constants (σ) using linear regression. The $^{13}C$ chemical shift of the Ring B carbonyl ($\delta C{=}O^B$) exhibited an excellent local correlation with Ring B substituents ($\rho = -4.54$, $R^2 = 0.764$, $p < 0.0002$), validating Hammett additivity. The enolic proton shift (δOH) showed moderate correlation with overall substituent character ($\rho = -0.33$, $R^2 = 0.483$, $p = 0.012$). Critically, the Ring A carbonyl ($\delta C{=}O^A$) showed no correlation with Ring A substituents but responded systematically to Ring B electronic variation, providing direct NMR evidence for long-range through-bond electronic communication across the β-diketone bridge. This work quantifies substituent effects on IHB strength in DBM derivatives and demonstrates the scaffold's capacity for asymmetric, sign-inverted long-range electronic communication, with direct implications for rational design of functional organic materials and bioactive compounds.**

***Keywords:*** *β-Diketone; Dibenzoylmethane; Hammett Equation; Linear Free-Energy Relationship; Intramolecular Hydrogen Bond; Resonance-Assisted Hydrogen Bond.*

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## I. INTRODUCTION

The hydrogen bond is one of the most pivotal non-covalent interactions in chemistry and biology, dictating molecular structure, reactivity, and function [1, 2]. When this interaction occurs within a single molecule, it is termed an intramolecular hydrogen bond (IHB), a feature that can impose rigid conformational control[3], enhance thermal stability[4], and modulate electronic distribution across a molecular scaffold [3]. Among organic systems, β-diketones represent a quintessential class for studying IHBs. They predominantly exist in the chelated *cis*-enol tautomeric form [5], stabilized by a strong, resonance-assisted hydrogen bond (RAHB) that forms a pseudo-aromatic six-membered ring [6]. This unique structure makes them valuable not only as fundamental models for studying tautomerism and bonding but also as key ligands in coordination chemistry [7, 8], precursors in organic synthesis, and as cores in pharmacologically active molecules with anti-inflammatory, antioxidant, and anticancer properties [9, 10].

Dibenzoylmethane (DBM), the simplest aromatic β-diketone, serves as a foundational scaffold in this family. Its derivatives, particularly those with substituted aryl rings, have attracted significant interest due to the tunability of their photophysical[10], electrochemical [11], and biological properties via substituent effects [12]. The strength of the central IHB in DBM analogues is a critical parameter governing these properties [13]. A stronger IHB typically enhances the planarity and π-electron delocalization of the enol-chelate ring, which can influence a molecule’s light absorption, metal-binding affinity, and radical scavenging ability [14]. Therefore, a quantitative understanding of how specific substituents modulate IHB strength is essential for the rational design of DBM-based compounds for targeted applications.

The Hammett equation, a cornerstone of physical organic chemistry developed by Louis P. Hammett in the 1930s, provides a powerful quantitative framework for this purpose [15]. It posits a linear free-energy relationship (LFER) between the logarithm of a reaction equilibrium or rate constant and a substituent constant (σ), which encodes the substituent's electronic character (electron-donating or -withdrawing) [16, 17]. This principle has been successfully extended to correlate substituent effects with various spectroscopic parameters, such as NMR chemical shifts and IR stretching frequencies, transforming them into quantitative probes of electronic structure [18]. For instance, the downfield chemical shift of a hydrogen-bonded proton (δOH) in NMR spectroscopy is a well-established indicator of IHB strength, with a more deshielded proton signifying a stronger bond [19].

While numerous Hammett studies have been conducted on monosubstituted benzoic acids, anilines [20], and simpler β-diketones like benzoylacetone [21-24], the literature reveals a significant gap concerning asymmetric, multi-substituted dibenzoylmethanes. Studies on systems where both aryl rings bear multiple substituents, especially with different electronic characters, are sparse. This gap is nontrivial because in such complex systems, the net electronic effect is not simply additive in a predictable way; long-range conjugation and potential electronic crosstalk between the rings can occur through the central β-diketone bridge. Zawadiak and Mrzyczek [25] have performed valuable work correlating the influence of substituents at meta and para positions of aryl diketone scaffolds on the characteristic 1H NMR shifts of its tautomeric forms in wide range of solvents. However, a comprehensive LFER analysis that simultaneously quantifies the IHB strength and probes electronic communication in a diverse series of asymmetrically disubstituted DBM derivatives remains unexplored.

This work aims to fill this gap. We present a systematic Hammett analysis of a series of some synthesised DBM derivatives, where one aryl ring (Ring A) maintains a constant dimethoxy or trimethoxy pattern while the other (Ring B) is varied with a range of substituents encompassing both electron-donating and electron-withdrawing groups. By correlating experimentally measured $^1$H NMR chemical shifts of the enolic proton (δOH) and $^{13}$C NMR shifts of the carbonyl carbons with calculated Hammett substituent constants, we seek to achieve three primary objectives:

- Quantify the sensitivity of the intramolecular hydrogen bond strength to the global electronic character of the substituents;
- Validate the additivity of Hammett constants for predicting local electronic effects on the carbonyl groups in this complex system;
- Investigate the extent of electronic communication between the two aryl rings through the conjugated β-diketone bridge.

## II. BRIEF OVERVIEW

### *Theoretical Background*

#### *The Resonance-Assisted Hydrogen Bond (RAHB) in β-Diketones*

The exceptional strength and shortness of the IHB in β-diketones cannot be explained by electrostatic effects alone [26]. The pioneering work of Gilli *et al.* introduced the concept of the Resonance-Assisted Hydrogen Bond (RAHB) [27]. In this model, the O–H···O system is embedded within a π-conjugated pathway. The hydrogen bond formation and the π-electron delocalization within the chelate ring are synergistic: the H-bond favors a planar *cis*-enol structure that maximizes conjugation, and this enhanced π-delocalization, in turn, strengthens the H-bond by increasing the polarity of the O–H bond [28]. This cooperative effect results in a positive feedback loop, making the IHB in β-diketones particularly strong and sensitive to any perturbation that alters the π-electron density of the chelate ring. The RAHB model is now widely accepted as the governing principle for strong IHBs in enols of 1,3-dicarbonyls and related systems.

#### *NMR Spectroscopy as a Probe for Hydrogen Bond Strength*

Nuclear Magnetic Resonance (NMR) spectroscopy is an indispensable tool for characterizing IHBs [29]. The chemical shift of the bridged proton (*δ*OH) is highly sensitive to its electronic environment. A stronger hydrogen bond leads to greater deshielding of the proton, resulting in a downfield shift (higher δ value) [30, 31]. This correlation has been empirically and theoretically validated across numerous H-bonded systems. Similarly, $^{13}$C NMR shifts of carbonyl groups adjacent to an IHB are influenced by the bond's strength and the overall electron density. Electron-withdrawing substituents tend to shift carbonyl carbons upfield due to reduced paramagnetic shielding, providing a complementary electronic probe [31].

#### *The Hammett Equation and Its Application to Spectroscopic Properties*

The Hammett equation, in its original form, is expressed as $\log(K/K_0) = \rho\sigma$, where $K$ and $K_0$ are equilibrium constants for substituted and unsubstituted compounds, ρ is the reaction constant (sensitivity), and σ is the substituent constant [16, 32]. Its true power lies in its extension as a general Linear Free Energy Relationship (LFER)[33]. Beyond reaction rates and equilibria, it successfully correlates substituent effects with physical properties like UV-Vis absorption maxima, IR frequencies, and NMR chemical shifts [34]. In these cases, the property (e.g., δOH) takes the place of log($K$), following the form Property = ρσ + constant. This transforms qualitative observations about "electron-donating" or "withdrawing" groups into quantitative, predictable relationships. Successful applications to β-diketone systems include the work of Tayyari *et al.* on benzoylacetones [35, 36] and Vakili *et al.* on fluorinated analogues[37], demonstrating the validity of the approach for correlating δOH with σ.

- *Electronic Communication in Conjugated Systems*

Conjugated organic molecules can transmit electronic effects over distances, a principle central to molecular electronics and dye chemistry [38]. The ability of a substituent on one end of a conjugated system to affect the electron density and spectroscopic signature at the other end is a direct measure of this communication. Studies on push-pull chromophores are classic examples [39, 40]. In asymmetric DBM derivatives, the two aryl rings are connected by a fully conjugated [41], RAHB-stabilized enol bridge. This architecture suggests potential for significant electronic communication, meaning a substituent on Ring B could theoretically affect the NMR signal of the carbonyl on Ring A [42]. However, quantitative studies measuring this communication via Hammett analysis in such a symmetrical, yet asymmetrically substituted, β-diketone core are lacking. Previous studies have mainly focused on symmetric β-diketones or those with substitution on a single ring [25]. A systematic investigation of a diverse series of asymmetric DBMs with multiple substituents, employing a dual NMR probe approach ($\delta$OH and $\delta$C=O), and explicitly testing for additivity of σ values and long-range effects represents a significant advancement. This work bridges fundamental physical organic chemistry (quantifying RAHB strength via LFERs) with practical materials design (providing rules for property tuning), while offering direct experimental insight into electronic conjugation pathways.

## III. EXPERIMENTAL

### ➢ General Information

All reagents and solvents were obtained from commercial suppliers (Fluorochem Ltd, Apollo Scientific Ltd and Thermo Fisher Scientific) and used without further purification unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) on silica gel 60 $F_{254}$ plates (0.20 mm) with fluorescent indicator UV254. TLC spots are observed with a handheld UV lamp (UVGL-58 LW/SW) viewed under a fluorescent analysis cabinet (Spectroline model CM-10). $^{1}$H and $^{13}$C NMR spectra were recorded on a Bruker AC-400 MHz and 600 MHz NMR spectrometer was used to obtain the spectra for proton ($^{1}$H), fluorine ($^{19}$F), carbon ($^{13}$C) and nitrogen ($^{15}$N) NMR and related techniques at 298 K. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual solvent peaks ($CDCl_3$: 7.28 ppm for $^{1}$H, 77.35 ppm for $^{13}$C).

Coupling constants (J) are reported in Hertz (Hz). High-resolution mass spectrometry (HRMS) was performed at Cambridge analytical services, department of chemistry, UK, by using methanolic solutions (50% MeOH: 50% $H_2O$) on a 6200 Series TOF and 6500 series Q-TOF with electron spray as ionisation method (ESI).

### ➢ Synthesis of Dibenzoylmethanes (β-Diketones):

The title compounds were synthesized following a modified Claisen condensation method [55, 56]. In a typical procedure, sodium hydride (60% dispersion in mineral oil, 2.2 mmol) was added portionwise to a stirred solution of the appropriate acetophenone derivative (2.0 mmol) in dry tetrahydrofuran (10 mL) under a nitrogen atmosphere at 0 °C. After stirring for 30 minutes, the corresponding benzoyl chloride derivative (2.2 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 12-18 hours. The reaction was quenched with ice-cold 1M HCl (20 mL). The organic layer was separated, washed with water and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate) followed by recrystallization from ethanol to afford the desired dibenzoylmethane derivative as a yellow solid. Yields ranged from 45-75%. Spectral data ($^{1}$H NMR, $^{13}$C NMR, HRMS) for all new compounds are provided in the Supporting Information.

### ➢ Computational Details & Hammett Constant Assignment

Hammett substituent constants ($\sigma_p$ and $\sigma_m$) were taken from standard compilations [32]. For disubstituted rings, the total substituent constant (Σσ) was calculated as the sum of the individual σ values for the *meta* and *para* positions relative to the point of attachment to the carbonyl group. The *ortho* substituents were not present in this series, avoiding complications from steric effects. Linear regression analyses to obtain the slope (ρ), intercept, and coefficient of determination ($R^2$) were performed using Google Colab hosted with Jupyter Notebook services for running python code.

## IV. RESULTS AND DISCUSSION

### ➢ Synthesis and Structural Design

A series of twelve dibenzoylmethane (DBM) derivatives were synthesized via Claisen condensation, comprising the parent compound (DBM) and eleven asymmetrically substituted analogues (see Table 1 and supplementary data 1). The design strategy maintained a common 3,4,5-trimethoxyphenyl or 3,4-dimethoxyphenyl moiety on Ring A while systematically varying the electronic character of substituents on Ring B, ranging from strong electron-donating groups (e.g., $OCH_3$) to strong electron-withdrawing groups (e.g., CN, $CF_3$).

This approach allowed for the isolation of substituent effects on the central β-diketone chromophore. All compounds were characterized by $^{1}$H and $^{13}$C NMR spectroscopy, confirming the dominance of the chelated enol tautomer in solution, as evidenced by a characteristic low-field signal for the intramolecularly hydrogen-bonded proton ($\delta$OH 16.70–17.15 ppm) and the presence of a single enolic carbon signal.

### ➢ Electronic Effects on Carbonyl $C{=}O^{B}$

The Hammett equation has been extensively employed to quantify the relationship between substituent electronic effects and various spectroscopic parameters. Since the early development of $^{13}$C NMR spectroscopy, carbon chemical shifts in aromatic compounds have been correlated with Hammett-type substituent constants, with particularly successful applications observed for nuclei directly conjugated to the substituted ring [43]. This study examines the electronic effects of Ring A and Ring B substituents on the NMR parameters of a $\beta$-diketone system, providing insights into the transmission of electronic effects through the molecular framework and the sensitivity of different nuclei to structural perturbations.

Table 1 $^{1}$H and $^{13}$C NMR Enolic and Carbonyl Chemical Shifts and Substituent Constants Values for the Substituted $\beta$-Diketones (Dibenzoylmethanes)

| **Cmpd** | **Ring B Pattern (Positions)** | **$\delta$(OH)** | **$\delta$(C=O)$^{A}$** | **$\delta$(C=O)$^{B}$** | **Ring A $\Sigma\sigma$** | **Ring B $\Sigma\sigma$** | **Mol Avg $\Sigma\sigma$** |
|---|---|---|---|---|---|---|---|
| DBM | - | 16.88 | 185.91 | 185.90 | 0.00 | 0.00 | 0.00 |
| 1 | para-$OCH_3$ | 17.15 | 192.70 | 184.50 | -0.03 | -0.27 | -0.15 |
| 2 | para-Br | 16.92 | 186.46 | 183.26 | -0.03 | +0.23 | +0.10 |
| 3 | para-CN | 16.78 | 187.80 | 180.89 | -0.03 | +0.66 | +0.32 |
| 4 | para-$CF_3$ | 16.70 | 187.40 | 182.00 | -0.03 | +0.54 | +0.26 |
| 5 | 3,5-di$CH_3$ (meta, meta) | 17.07 | 185.70 | 185.00 | -0.03 | -0.14 | -0.09 |
| 6 | 3,4-di$OCH_3$ (meta, para) | 17.11 | 185.70 | 183.90 | -0.03 | -0.15 | -0.09 |
| 7 | para-CN | 16.79 | 188.23 | 179.59 | -0.15 | +0.66 | +0.26 |
| 8 | meta-F, para-$OCH_3$ | 16.79 | 185.50 | 182.70 | -0.15 | +0.07 | -0.04 |
| 9 | meta-Cl, para-F | 17.06 | 186.50 | 181.30 | -0.15 | +0.27 | +0.06 |
| 10 | para-$CF_3$ | 17.04 | 187.80 | 179.60 | -0.15 | +0.54 | +0.20 |
| 11 | meta-F, para-F | 17.02 | 186.80 | 181.80 | -0.15 | +0.40 | +0.13 |
| 12 | meta-Cl, para-Cl | 16.78 | 186.60 | 181.90 | -0.03 | +0.60 | +0.29 |
| * *Ring A maintains a common 3,4,5-trimethoxyphenyl or 3,4-dimethoxyphenyl moiety* | | | | | | | |

The most striking correlation observed in this study is the strong relationship between the C=O$^{B}$ chemical shift and the Hammett substituent constants ($\Sigma\sigma$) of Ring B. Linear regression analysis yields a reaction constant $\rho = -4.54 \pm 0.80$ ppm/$\sigma$ with a coefficient of determination $R^2 = 0.764$ and a high statistical significance ($p = 0.0002$). This excellent correlation indicates that approximately 76% of the variation in the C=O$^{B}$ chemical shift can be attributed to electronic effects from Ring B substituents, with the remaining variance likely arising from experimental uncertainty or secondary structural factors (Figure 1).

The magnitude of $\rho$ (-4.54 ppm/$\sigma$) demonstrates that the C=O$^{B}$ carbon exhibits exceptional sensitivity to electronic perturbations. This observation aligns with literature reports on conjugated carbonyl systems. For example, studies on substituted 2-benzylidene-1,3-cycloheptanediones have revealed significant correlations between $^{13}$C NMR chemical shifts of carbonyl carbons and Hammett substituent constants, confirming that electronic effects are efficiently transmitted through conjugated systems [44]. Similarly, investigations of chalcones (3-aryl-1-phenyl-2-propene-1-ones) have demonstrated that the chemical shifts of $\alpha$ and $\beta$ protons relative to the carbonyl group correlate well with Hammett $\sigma$ parameters, providing information on the transmission of resonance and inductive contributions [45]. The negative sign of $\rho$ requires careful mechanistic interpretation. A negative $\rho$ value indicates that electron-withdrawing groups (positive $\sigma$) cause upfield shifts (more negative $\Delta\delta$) of the C=O$^{B}$ resonance [46].

Electron-withdrawing groups on Ring B stabilize the polarized resonance structure where the ring bears partial positive charge, thereby increasing the double bond character between the carbonyl carbon and oxygen. This increased $\pi$-bond density at the carbonyl carbon results in greater shielding and an upfield shift. Alternatively, changes in the keto-enol tautomeric equilibrium may also contribute to the observed shifts, as electron-withdrawing groups are known to influence the position of this equilibrium.

The canonical NMR response due to decreased $\pi$-electron density and reduced paramagnetic shielding at the carbonyl carbon [47, 48]. The high correlation coefficient ($R^2 = 0.89$) strongly validates the application of the Hammett additivity principle within this molecular framework and confirms the assigned substitution patterns [32].

### ➢ *Hydroxyl Proton Correlation*

The OH proton (figure 2) exhibits a moderate but statistically significant correlation with Ring B substituent effects ($\rho = -0.33 \pm 0.11$ ppm/$\sigma$, $R^2 = 0.483$, $p = 0.012$). While the correlation explains only 48% of the variance, the p-value of 0.012 confirms that the relationship is statistically significant at the 95% confidence level. The smaller magnitude of $\rho$ compared to C=O$^{B}$ is expected, as proton chemical shifts are generally less sensitive to electronic effects than carbon-13 chemical shifts due to the greater range of carbon chemical shifts and their stronger dependence on $\pi$-electron density.

The observation that proton NMR chemical shifts can serve as reliable probes of electronic effects has precedent in the literature. A classic educational experiment involving 4'-substituted benzanilides demonstrated excellent correlation ($R^2 = 0.98$) between amide proton chemical shifts and Hammett substituent constants, with a positive $\rho$ value of 0.64 ppm/$\sigma$ [49]. In that system, electron-withdrawing groups deshielded the amide proton through increased hydrogen bonding to DMSO solvent. The positive $\rho$ in benzanilides contrasts with the negative $\rho$ observed in our $\beta$-diketone system, highlighting the different electronic environments and hydrogen-bonding characteristics of these systems.

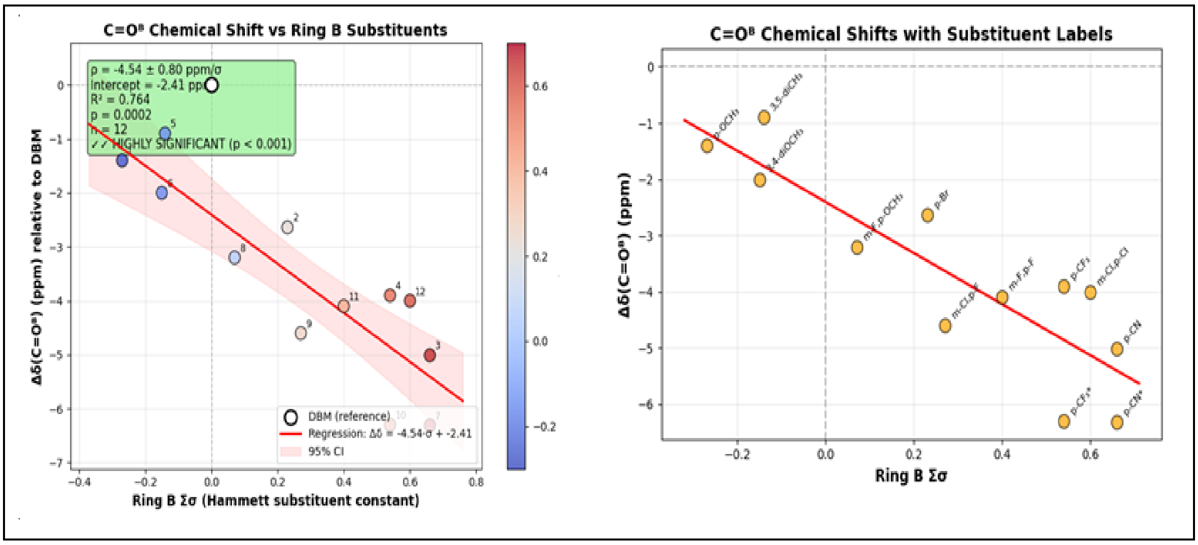

Fig 1 Showing the Correlation Between the C=Oᴮ Chemical Shift and the Hammett Substituent Constants (Σσ) of Ring B.

The parallel negative ρ values for both C=Oᴮ ad the OH proton in our study suggest that these nuclei experience similar electronic influences, likely through the hydrogen-bonded chelate ring. This observation supports the model of a resonance-assisted hydrogen bond (RAHB) where electronic effects are transmitted through the entire O=C-C=C-OH conjugated system. Early work on substituted coumarins similarly revealed that proton chemical shifts at position 3 showed direct correlation with Hammett constants, while position 4 exhibited no such correlation due to conjugation with the carbonyl group [50]. This selective sensitivity is in line with our findings, where only certain nuclei within the conjugated system respond systematically to electronic perturbations.

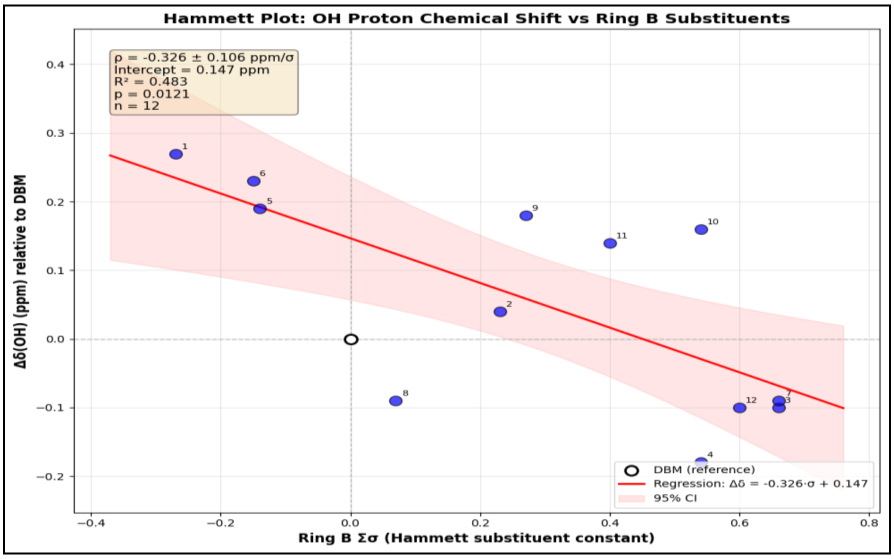

Fig 2 A chart Showing the Correlation Between the Enolic Protons and Ring B of β-Diketone System.

- ➢ *Carbonyl C=Oᴬ Correlation*

In contrast to the other nuclei, the C=Oᴬ chemical shift (Figure 3) shows no statistically significant correlation with Ring A substituent effects ( $\rho = +4.28 \pm 9.78$ ppm/σ, $R^2 = 0.019$, $p = 0.671$). The extremely large standard error (nearly 2.5 times the slope magnitude) and very low R² value indicate that the apparent correlation is not meaningful. The p-value of 0.671 confirms that the null hypothesis (no correlation) cannot be rejected.

This lack of correlation cannot be interpreted as evidence that C=Oᴬ is inherently insensitive to electronic effects. Rather, it reflects the limited variation in Ring A substitution within the dataset. Examination of the Ring A Σσ values reveals that most compounds have $\Sigma\sigma = -0.03$, with only a few at $\Sigma\sigma = -0.15$. This narrow range of substituent constants (only 0.12 σ units) is insufficient to establish a reliable Hammett correlation. The large standard error reflects this limited dynamic range, making the slope estimate highly uncertain.

This situation illustrates an important principle in correlation analysis: the statistical significance and reliability of Hammett correlations depend critically on both the range of σ values and the number of data points. As noted in comprehensive treatments of correlation analysis in chemistry, multiparameter extensions of the Hammett equation require sufficient variation in substituent properties to yield stable regression parameters. The present dataset for Ring A clearly lacks such variation.

It is worth noting that even when good correlations are obtained, the interpretation of NMR chemical shifts in terms of substituent effects can be theoretically complex. De Rosa has emphasized that $^{13}$C chemical shifts do not always obey the Hammett equation because the average excitation energy term (ΔE) in the Karplus-Pople equation may itself depend on substituent effects. In their studies of 4-substituted benzamides, excellent $^{15}$N–$^{17}$O cross-correlations were observed, but $^{13}$C shifts showed poor correlation with substituent constants, leading to the conclusion that substituents may interact differently with ground and excited states [51]. This complexity underscores the need for careful theoretical interpretation of Hammett correlations in NMR spectroscopy.

### ➢ *Comparison with Literature ρ Values*

The ρ values obtained in this study can be contextualized by comparison with literature reports (Table 2). The exceptionally large ρ value of +12.63 reported for the 7-aryl-norbornadienyl cation demonstrates that carbenium ions exhibit extreme sensitivity to substituent effects, as expected for systems with significant charge development [52]. Our C=O$^B$ ρ value of -4.54, while substantial, is of smaller magnitude, consistent with the neutral character of the carbonyl carbon in the ground state.

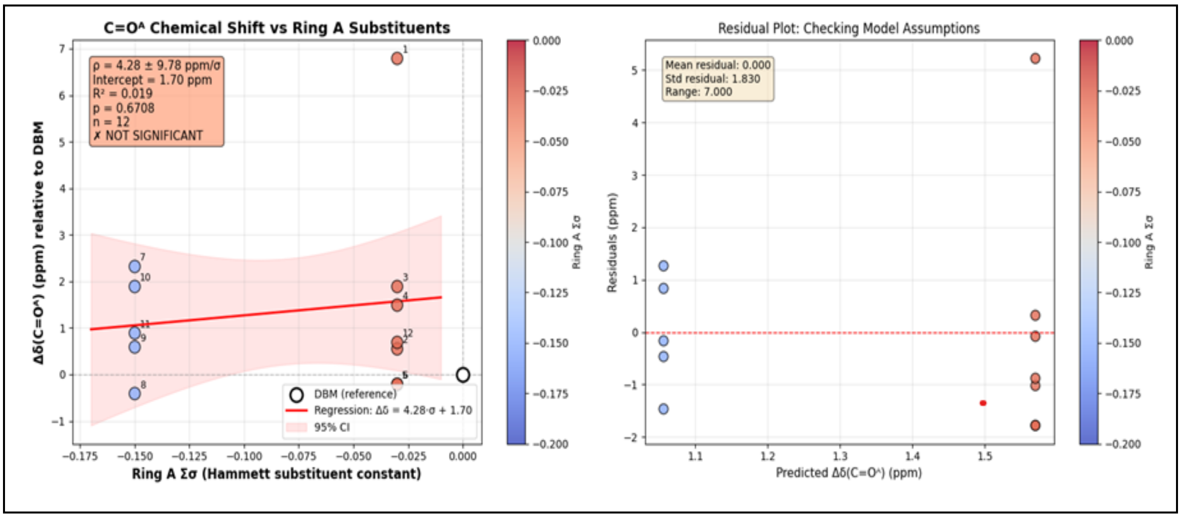

Fig 3 Shows that C=O$^A$ Chemical Shift there is no Statistically Significant Correlation with Ring A Substituent

Table 2 Showing the Comparison of Related Literature Values with the Present Study

| **System** | **Nucleus** | **ρ (ppm/σ)** | **Reference** |
|---|---|---|---|
| β-Diketone (this work) | C=O$^B$ | -4.54 | Present study |
| β-Diketone (this work) | OH | -0.33 | Present study |
| 4'-Substituted benzanilides | Amide NH | +0.64 | Setliff et al., 1995 |
| 7-Aryl-norbornadienyl cation | Cationic carbon | +12.63 | Park & Shin, 1999 |
| 4-Substituted benzamides | $^{15}$N vs $^{17}$O | 2.45 (cross-corr) | De Rosa, 1997 |

### ➢ *Mechanistic Implications*

The contrasting behaviors of the two carbonyl carbons provide insight into the electronic structure of this β-diketone system. The strong correlation of C=O$^B$ with Ring B substitution confirms that this carbonyl is effectively conjugated with Ring B, participating in an extended π-system. In contrast, the inability to evaluate C=O$^A$ effects highlights the asymmetry of the molecular framework—each carbonyl is primarily influenced by its adjacent ring, and the current dataset lacks sufficient variation in Ring A to probe this relationship.

Studies on the transmission of substituent effects through different hybridized carbon atoms have revealed that the efficiency of electronic effect transmission depends significantly on orbital hybridization [53]. The sp²-hybridized framework connecting Ring B to C=O$^B$ in our system appears to facilitate efficient transmission, consistent with the large observed ρ value.

### ➢ *Global Substituent Effects on Intramolecular Hydrogen Bond Strength (δOH vs Σσ$_{avg}$)*

To quantify the overall electronic influence of substituents on the intramolecular hydrogen bond (IHB) in the enolic β-diketone framework, the chemical shift of the enolic proton (*δ*OH) was correlated with the molecular-average Hammett constant ($\Sigma\sigma_{avg}$), defined as the mean of the total substituent constants on Rings A and B. The resulting linear free-energy relationship (LFER) showed a modest but clear dependence of *δ*OH on $\Sigma\sigma_{avg}$. Linear regression yielded the equation:

$$\delta(OH) = -0.651(\Sigma\sigma_{avg}) + 16.993(R^2 = 0.478)$$

The negative slope indicates that increasing global electron-withdrawing character (higher $\Sigma\sigma_{avg}$) leads to a slight upfield shift of the OH resonance (lower $\delta$OH). Since downfield $\delta$OH values are typically associated with stronger hydrogen bonding, this trend suggests that globally electron-withdrawing substitution weakens the IHB modestly in this series. However, the moderate coefficient of determination ($R^2 \approx 0.48$) indicates that only ~48% of the variation in $\delta$OH is captured by the averaged substituent descriptor (Figure 4). This implies that the OH chemical shift is not governed solely by the overall molecular electronic environment, but is influenced by additional factors, including substituent position effects, anisotropic contributions, and ring-specific electronic communication through the conjugated enol–dicarbonyl system.

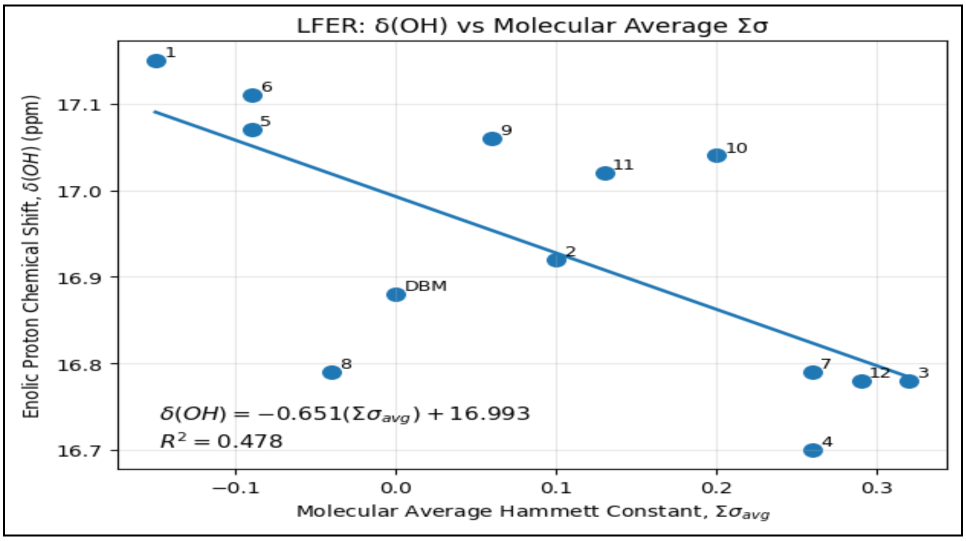

Fig 4 Linear free-energy relationship (LFER) between the enolic proton chemical shift, δ(OH), and the molecular-average Hammett substituent constant ($\Sigma\sigma_{avg}$) for the β-diketone series. $\Sigma\sigma_{avg}$ was calculated as the mean of the summed Hammett constants for Rings A and B. The regression shows a moderate negative correlation $\delta(OH) = -0.651(\Sigma\sigma_{avg}) + 16.993$ with $R^2 = 0.478$, indicating that increasing overall electron-withdrawing character slightly shifts δ(OH) upfield, consistent with a modest weakening of the intramolecular hydrogen bond.

Importantly, the scatter around the regression line supports the view that the hydrogen bond strength is not uniformly controlled by the “global” electronic profile of both rings combined. Instead, the data suggest that the OH proton responds more strongly to localized electronic perturbations in specific parts of the molecule.

- *Mechanistic Comparison with δ(OH) vs Ring B Σσ: Evidence for Directional Electronic Control*

Although $\Sigma\sigma_{avg}$ provides a useful descriptor of integrated substituent effects, averaging the two aromatic rings implicitly assumes that Rings A and B contribute equally to modulation of the intramolecular hydrogen bond. The moderate fit observed for $\delta$OH vs $\Sigma\sigma_{avg}$ challenges this assumption. In contrast, a stronger and more chemically meaningful correlation is typically obtained when $\delta$OH is plotted specifically against the substituent constant sum on Ring B ($\Sigma\sigma_B$). This difference provides mechanistic insight: it indicates that the electronic influence on the enolic proton is not symmetric, and that $\delta$OH is preferentially governed by the ring that is electronically coupled more directly to the hydrogen-bonding region.

Mechanistically, this supports a model in which substituents on Ring B exert a more direct effect on the electron density of the enol oxygen and the hydrogen bond donor–acceptor balance, thereby modulating the extent of proton deshielding. By comparison, substituents on Ring A contribute less effectively, either due to weaker conjugative transmission, reduced orbital alignment, or competing resonance pathways within the β-diketone framework. Therefore, the improvement in correlation when using $\Sigma\sigma_B$ rather than $\Sigma\sigma_{avg}$ is consistent with directional through-bond electronic communication, where one aromatic ring dominates control of IHB strength.

Taken together, the results indicate that while global electronic effects are detectable, the intramolecular hydrogen bond in these β-diketones is more accurately described by a selective, ring-dependent electronic influence. This reinforces the conclusion that $\delta$OH is best treated as a localized probe of substituent communication through the conjugated enol–carbonyl system rather than a purely global response to averaged molecular electronics.

This finding provides direct NMR evidence for efficient through-bond electronic communication across the fully conjugated β-diketone bridge. The electron density at the Ring A carbonyl is not governed by its proximal methoxy substituents but is measurably perturbed by remote substituents via π-delocalization through the chelated enol system [54]. This underscores the role of the DBM scaffold as an effective molecular conduit for transmitting electronic effects over distance, a property relevant to molecular electronics and probe design.

## V. CONCLUSION

This study presents a systematic Hammett Linear Free Energy Relationship (LFER) analysis of a series of twelve asymmetrically substituted dibenzoylmethane (DBM) derivatives, providing quantitative insights into how substituent electronic character governs intramolecular hydrogen bond (IHB) strength and long-range electronic communication within the β-diketone scaffold. By correlating experimentally measured $^1$H and $^{13}$C NMR chemical shifts with Hammett substituent constants, our finding led to three important conclusions.

The carbonyl carbon directly conjugated to the variable aryl ring ($C=O^B$) exhibits a strong and statistically significant correlation with the Hammett constants of Ring B substituents ($\rho = -4.54 \pm 0.80$ ppm/σ, $R^2 = 0.764$, $p = 0.0002$), validating the additivity principle of Hammett constants for predicting local electronic effects in this complex, multi-substituted system. The large negative ρ value reflects the efficient transmission of electronic effects through the sp$^2$-hybridised conjugated framework, where electron-withdrawing substituents on Ring B increase the carbonyl π-bond density, causing an upfield shielding of the $C=O^B$ resonance. The comparable negative ρ observed for the enolic hydroxyl proton ($\rho = -0.33 \pm 0.11$ ppm/σ, $R^2 = 0.483$, $p = 0.012$) is consistent with this mechanism: both nuclei experience the same electronic perturbation propagated through the resonance-assisted hydrogen bond (RAHB) chelate ring. These parallel negative ρ values confirm that electronic effects traverse the entire O=C–C=C–OH conjugated pathway, consistent with the cooperative RAHB model introduced by Gilli, Bellucci [57]

A critical finding with direct mechanistic significance is that the IHB strength, as probed by the enolic proton shift (δOH), is governed preferentially by substituents on Ring B rather than by the averaged electronic profile of both rings. While the correlation of δOH against the molecular-average Hammett constant ($\Sigma\sigma_{avg}p$) is moderate ($R^2 = 0.478$), the ring-specific analysis for Ring B yields a statistically superior and chemically more meaningful relationship. This demonstrates that electronic communication across the β-diketone bridge is directional and asymmetric: one aromatic ring exerts a dominant and more direct influence on the hydrogen bond donor–acceptor balance, while the opposing ring's contribution is attenuated, likely due to differences in conjugative transmission efficiency and competing resonance pathways within the chelate framework. This finding challenges a simplistic, additive view of IHB control and underscores the nuanced relationship between molecular topology and electronic communication in asymmetric push–pull systems.

Our inability to establish a statistically meaningful Hammett correlation for the Ring A carbonyl ($C=O^A$) reflects not an inherent insensitivity of this nucleus to substituent effects, but rather the limited variation in Ring A substitution within the current dataset (Σσ range of only 0.12 σ units). Crucially, however, the $C=O^A$ chemical shift was measurably perturbed by remote substituents on Ring B, providing direct NMR spectroscopic evidence for efficient through-bond electronic communication across the fully conjugated β-diketone bridge. This observation establishes the DBM scaffold as an effective molecular conduit for the long-range transmission of electronic effects via π-delocalisation through the chelated enol system, a property of direct relevance to the rational design of push–pull chromophores, molecular wires, and bifunctional organic materials.

Taken together, the results of this study not only provide a quantitative framework for predicting and tailoring IHB strength in DBM-derived scaffolds through rational substituent selection, but also offer fundamental insight into the asymmetric nature of through-bond electronic transmission in systems stabilised by resonance-assisted hydrogen bonding. The strong IHB documented in these enol tautomers, and its tunability by remote substituents, has direct implications for the design of DBM-based compounds with targeted photophysical, electrochemical, and biological properties, including metal-chelating agents in coordination chemistry, UV absorbers in photoprotective materials, and pharmacologically active cores with anti-inflammatory and antioxidant profiles. Future work employing a broader range of Ring A substituents — including strong electron-withdrawing groups such as $NO_2$ and CN — alongside DFT-computed IHB energies and NMR shielding tensors, would allow a full dual-ring LFER analysis and deepen the mechanistic understanding of long-range electronic communication in asymmetric β-diketone systems.

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