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A STUDY OF HYPERCONJUGATION EFFECTS IN THE 1,4-DI-*p*-TOLYLBUTANE-1,4-DIONE STRUCTURE

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Planar 1,4-di-p-tolylbutane-1,4-dione was synthesized via one-flask $ZnCl_2 \cdot Et_3N \cdot t\text{-BuOH}$ mediated cascade condensation of 4-methylacetophenone and 2-bromo-4'-methylacetophenone. Non-covalent interactions have been analyzed in the solid state from crystal analysis data. Moreover, the hyperconjugation effects in this molecule and n-butane as model have been investigated and compared employing the density functional theory (DFT) and potential energy scans.

Keywords: hyperconjugation, 1,4-di-p-tolylbutane-1,4-dione, density functional theory, potential energy scans, X-ray analysis.

An understanding of the rotation barrier of organic compounds is fundamental for structural theory and the conformational analysis and requires the consistent theoretical models as well as experimental results to differentiate the steric and hyperconjugation effects [1].

It is well known that a hyperconjugation in neutral hydrocarbons is a critical effect for a prediction of possible conformers [2]. For example, the staggered conformer of ethane is most stable. From potential energy (PES) scan of ethane, this had no connection to the amount of electrostatic repulsions within the molecule. These results demonstrate that Coulombic forces do not explain the favored staggered conformations [3]. Moreover, a prediction of molecular structure in the solid and solution state is a key in the material chemistry [4, 5] as well as in an investigation of the chiroptical properties of various compounds [6, 7].

Single crystals of 1,4-di-p-tolylbutane-1,4-dione were grown from isopropyl alcohol by slow solvent evaporation. The crystal structure from a crystallography analysis is displayed in Fig. 1. The crystal system and space group was determined to be monoclinic and $P2_1/n$, respectively. The aromatic p-tolyl moieties are located in a parallel to each other and

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partially overlapped. The dihedral angle between them is 0.00° was estimated from X-ray analysis as well as from optimized structure using DFT. In addition, the energies (E_i) of intermolecular interactions in the D1-3 dimers were estimated employing the basis set superposition effect. Due to the parallel structure, the strong face to face $\pi\cdots\pi$ stacking and C-H$\cdots\pi$ intermolecular interactions are found (dimer D1 in Fig. 1). For the D1 dimer, the highest interaction energy was estimated to be -58.4 kJ mol^{-1}. Moreover, a close side to side C-H$\cdots$O hydrogen bond

between the methyl and carbonyl groups is indicated, which connects the $\pi\cdots\pi$ stacked structures (D2 in Fig. 1). For this dimer, E_i of -22.9 kJ mol^{-1} was estimated. The D3 dimer with lowest interactions energy of -8.0 kJ mol^{-1} connects only with a weak C-H$\cdots$H-C hydrophobic London dispersion force (Fig. 1).
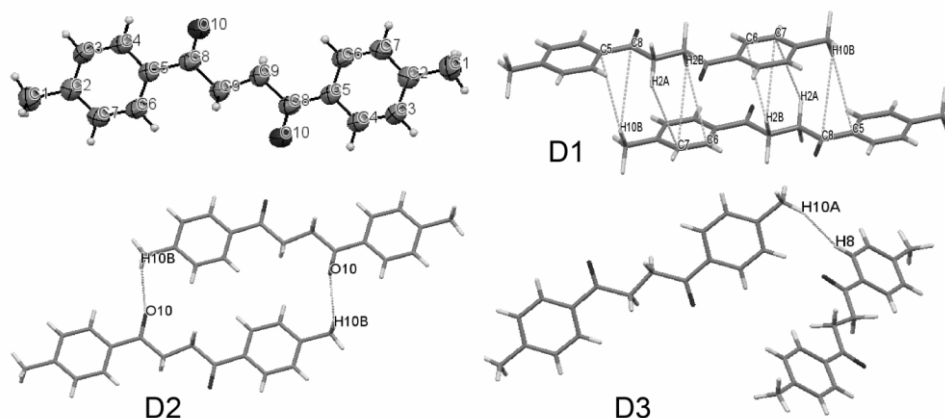

Fig. 1. Crystal structure (probability of ORTEP is 50 %) and intermolecular interaction between the 1,4-di-p-tolylbutane-1,4-dione molecules

To explain the parallel structure of 1,4-di-p-tolylbutane-1,4-dione, the barriers of rotation between the mid C9-C9' (R1 rotation) and conjugated p-tolyl- carbonyl bonds (R2 rotation) in 1,4-di-p-tolylbutane-1,4-dione as well as n-butane C2-C3 bond as model molecule were estimated using PES. For these calculations, high wB97X-D functional with the London dispersion corrections and 6-31G(d,p) basis set with the polarization functions on C and O atoms and hydrogen was used. First of all, from PES, most stable conformer of this molecule is the same as that obtained from X-ray data. Secondly, the higher full rotation barrier around the mid C9-C9' (R1 rotation) in the molecule than in n-butane was predicted to be 34.5 and 21.6 kJ mol^{-1} in the gas phase, respectively, due to a higher steric repulsion of the p-toluoyl than methyl moieties. However, the rotation barriers from the stable staggered to gauche conformations of 1,4-di-p-tolylbutane-1,4-dione (R1) and n-butane at angle of about 60° are 4.9 and 13.4 kJ mol^{-1}, respectively. Taking into account that the steric repulsion of moieties is not influenced for this rotation, the hyperconjugation effect in the n-butane is 2.7 times higher than in the 1,4-di-p-tolylbutane-1,4-dione case. This effect is called a negative hyperconjugation [8]. For example, Murakami et al. reported that boryl and silyl groups be-have as σ-acceptors and prefer to rotate inward in the cyclobutene ring-opening reaction despite the steric congestion [9]. For comparison, the rotation between conjugated p-tolyl-carbonyl bonds (R2 rotation) was estimated.

In this case, the barrier is 28.4 kJ mol^{-1} when p-tolyl and carbonyl moieties are particular to each other. In this case, it is possible to compare the energies in operation of hyperconjugation and conjugation of carbonyl and phenyl moieties. The energy of R2 rotation is 5.8 times higher than rotation energy of negative hyperconjugated mid C9-C9' (R1 rotation) was measured. In additional, vibrations between of angles using thermal energy (i.e. k_bT, where k_b is Boltzmann constant and T = 298 K) as a threshold of rotation at room temperature were indicated to be ±17° and ±33° for the n-butane/ R2 and R1 rotation of the corresponding molecule. Based on the theoretical and experimental data, the intermolecular interactions parallel the 1,4-di-p-tolylbutane-1,4-dione structure in the solid state because the interaction energies are much higher than the hyperconjugation effects.
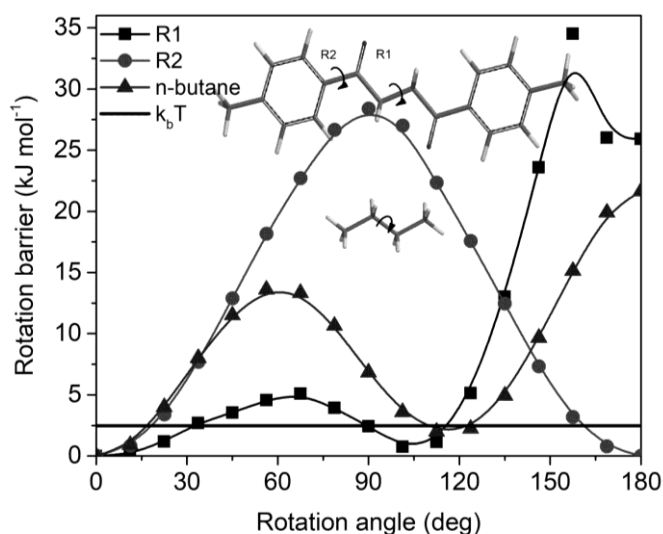

Fig. 2. PES scans of ground sates of 1,4-di-p-tolylbutane-1,4-dione
and n-butane (Line of k_bT energy is shown in black line)

Because the negative hyperconjugation causes an elongation of the σ-bond by adding electron density to its antibonding orbital, the bonding highest occupied (HOMO) and antibonding lowest unoccupied (LUMO) molecular frontier orbitals of 1,4-di-p-tolylbutane-1,4-dione and n-butane were generated and analyzed (Fig. 3). An electron density on antibonding LUMO is delocalised on the π* of conjugated p-toluoyl and small part of σ* orbitals of hydrogen of the central ethylene fragment. However, in the n-butane case, the electron density of LUMO exhibits on corresponding central ethylene fragment due to hyperconjugation of the C2-C3 bond. Density of the bonding HOMO orbitals of 1,4-di-p-tolylbutane-1,4-dione is delocalized on the n of carbonyl and σ orbitals of central ethylene fragment. This is well suited the negative hyperconjugation image.

In additional, a length of the central C9-C9' bond was estimated to be same value of 1.518 Å from X-ray data and DFT calculation, respectively. For comparison, the C2-C3 bond length of n-butane is 1.529 Å at the wB97X-D/6-31G(d,p) theory level. Due to accepting properties of p-toluoyl group, the C9-C9' bond length is lower to be 0.011 Å than corresponding bond in n-butane as model molecule.
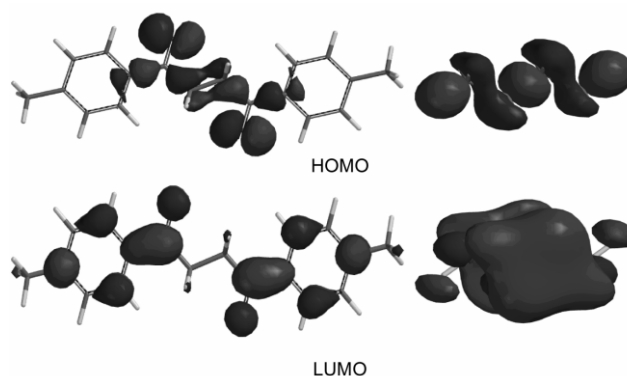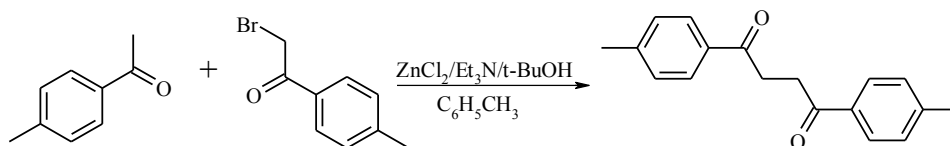
Fig. 3. Frontier HOMO and LUMO orbitals of 1,4-di-p-tolylbutane-1,4-dione
and n-butane (isovalue is 0.032)

1,4-Bis(4-methylphenyl)butane-1,4-dione was obtained by the method close to reported procedure [10].

Commercial anhydrous $ZnCl_2$ (0.14 g, 1.0 mmol) was placed into a one-neck, 25-mL round-bottom flask and dried by melting under vacuum (10-20 torr) at 250-350 °C for 15 min. After cooling under vacuum to r.t., toluene (1.4 mL), triethylamine (0.104 ml, 0.75 mmol), and *t*-BuOH (0.07 mL, 0.75 mmol) were successively added. The mixture was stirred until zinc chloride was fully dissolved (approx. 2 h), and 4-methylacetophenone (0.104 g, 0.75 mmol) and 4-methylphenacyl bromide (0.110 g, 0.5 mmol) were successively added. The mixture was stirred for 1 h, allowed to stand for 4 days at r.t., quenched with 5 % aq H_2SO_4 and filtered. Crystalline product were washed successively with benzene, H_2O and MeOH, and recrystallized from 2-propanol. The 1,4-di-p-tolylbutane-1,4-dione was obtained as white crystalline mass (mp = 158−160 °C).

Details of the crystal analysis

A colourless chip crystal of $C_{18}H_{18}O_2$ having approximate dimensions of 0.84 x 0.11 x 0.10 mm was mounted on a glass fibber. All measurements were made on a Rigaku XtaLAB mini diffractometer using graphite monochromated Mo-Kα radiation. The data were collected at a room temperature to a maximum 2θ value of 55.0^o. A total of 540 oscillation images were collected. The structure was solved by the SHELX97 method and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure crystallographic software package. For the intermolecular interactions visualization, the Mercury 3.7 program was used. CCDC 1587824 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Table 1

Data of crystal analysis of 1,4-di-*p*-tolylbutane-1,4-dione structure

Empirical Formula	$C_{18}H_{18}O_2$
Crystal Color, Habit	Colorless, chip
Crystal Dimensions	0.84 x 0.11 x 0.10 mm
Crystal System/Lattice Type	Monoclinic/Primitive
Lattice Parameters	a = 5.6184(10) Å
	b = 6.482(11) Å
	c = 20.08(3) Å
	β = 97.25(2)$^{\circ}$
	V = 725(2) Å^3
Space Group	$P2_1/n$ (#14)
Z value	2
D_{calc}	1.219 g/cm^3
R1[a]	0.0744
wR2[b]	0.2459

[a] R1 = Σ ||Fo| − |Fc|| / Σ |Fo|.

[b] wR2 = [Σ (w (Fo^2 − Fc^2)^2)/ Σ w(Fo^2)^2]$^{1/2}$

Details of the theoretical calculations

The geometry optimizations and single point energy calculations using density functional theory (DFT) in vacuum at 298 K temperature were performed. The geometry of the compound was optimized by the wB97X-D with the London dispersion corrections functional method and 6-31G(d,p) basis set. The intermolecular interaction energies between the molecules in dimers were estimated using the basis set superposition effect (BSSE) concept [11] and at wB97X-D functional and 6-31G(d,p) basis set. The dimers of molecule with intermolecular interactions from the X-ray analysis data were generated. The potential energy (PES) scans of molecule were conducted by rotating the corresponding moieties in steps of 10° from 0 to 180° employing the wB97X-D/6-31G(d,p) method. Full optimization of geometries was carried out in PES calculations. All DFT calculations were done with the Spartan'14 program in the gas phase [12].

The synthesized planar 1,4-di-p-tolylbutane-1,4-dione structure has been investigated using crystal analysis and DFT. From the theoretical calculations, a main reason of the structure planarization is intermolecular interactions in the solid state due to a low influence of hyperconjugation.

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ДОСЛІДЖЕННЯ ЕФЕКТУ ГІПЕРКОН'ЮГАЦІЇ В СТРУКТУРІ 1,4-ДІ-*n*-ТОЛІЛБУТАН-1,4-ДІОНУ

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Ротаційні бар'єри в органічних сполуках є одним з найголовніших чинників, які впливають на структурні особливості речовини у твердому стані. В свою чергу, просторове розміщення та конформація молекул у твердому стані вирішальним чином впливає на фізичні властивості матеріалів. Очевидно, що конформаційний аналіз органічних сполук є важливим інструментом, не тільки у теоретичному плані, а й має практичне значення для дослідження взаємозалежності структура – властивості. У цій роботі ми досліджували вплив стеричного ефекту та ефекту гіперкон'югації на конформацію модельної сполуки - 1,4-ди-*n*-толілбутан-1,4-діону. З цією метою отримано 1,4-ди-*n*-толілбутан-1,4-діон за допомогою однореакторної каскадної конденсації 4-метилацетофенону та 2-бромо-4'-метилацетофенону, каталізованої комплексом $ZnCl_2 \cdot Et_3N \cdot t\text{-BuOH}$. Реакція відбувається протягом 4 днів за кімнатної температури. Вирощено монокристал згаданого діону повільним випаровуванням розчинника з розчину ізопропанолу. Проаналізовано нековалентні взаємодії у твердому стані, опираючись на дані рентгеноструктурного аналізу. Побудовано теоретичні моделі димерів 1,4-ди-*n*-толілбутан-1,4-діону. Зроблено порівняльний аналіз ефектів гіперкон'югації для молекул отриманого дикетону та бутану з використанням теорії функціоналу густини (DFT) та зрізів потенціальної енергії (PES). З'ясовано, що головною причиною планарності 1,4-ди-*n*-толілбутан-1,4-діону у твердому стані є інтермолекулярні зв'язки у кристалічній решітці, а ефект гіперкон'югації відіграє другорядну роль. Всі теоретичні розрахунки проведено з використанням програми Spartan'14 в газовій фазі на рівні теорії густини функціоналу (DFT) методом wB97X-D/6-31G(d,p).

Ключові слова: гіперкон'югація, 1,4-ді-*пара*-толілбутан-1,4-діон, теорія функціоналу густини, зрізи потенціальної енергії, рентгеноструктурний аналіз.