Aryl-substituted derivatives of trimethylenemethane dianion: a dynamic NMR study

Roy Shenhar and Mordecai Rabinovitz *

Department of Organic Chemistry, The Hebrew University of Jerusalem, Givat-Ram, Jerusalem, Israel 91904

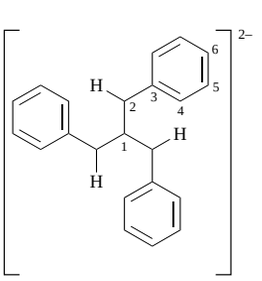
PERKIN 2 COMMUNICATION

Evidence is given for the structure of aryl-substituted trimethylenemethane dianions from NMR data, and the importance of p-π conjugation is discussed.

Cross-conjugated systems have been shown to possess a special stability compared to their linear analogues, and thus the parent trimethylenemethane dianion (TMM^{2-}) and its derivatives have become a focus of interest for the last several decades. Klein and Medlik[1] were the first to point out the facile formation of TMM^{2-} as the dilithium salt using *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) as a complexing agent.

Extensive theoretical work has been carried out to establish the geometry of TMM^{2-}, and to understand the reasons for its remarkable stability. The first exciting suggestion was that TMM^{2-} possesses a novel kind of aromaticity, coined 'Y aromaticity'[2] (that is feasible only when TMM^{2-} has a planar D_{3h} symmetry, making all four p-orbitals parallel to each other and thus enabling some kind of resonance through-the-centre), but this idea was doubted by Klein *et al.*,[3] who claimed internal Coulombic stabilization to be the dominating factor, and later by Wiberg,[4] who pointed out that TMM^{2-} has to cope with $6\pi e^-$ over only three C–C bonds (compared to benzene, with only $1\pi e^-$ per bond), and suggested that the stability of TMM^{2-} is due to its ability to distribute the extra charge to the three 'corners', thus minimizing the repulsive interactions. A support to Wiberg's explanation, based on *ab initio* calculations,[5] is found in the work of Frenking and co-workers,[5a] who reported TMM^{2-} to exist in a non-planar geometry with strongly pyramidal methylene groups. They have shown that the planar geometry previously suggested is a high-order saddle point, and that the conformations found to be the true minima are characterized by a strong shift of σ density towards the central carbon, with a concomitant counter-migration of π density to the terminal carbons, which is in accord with Wiberg's notion.[4]

Here we report an NMR study† of tribenzylidenemethane dianion (**1**)[6] and dibenzylidene-(3,5-dimethylbenzylidene)-methane dianion (**2**) with the aim of giving further insight into the ideas mentioned above.



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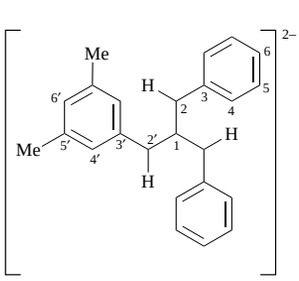

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† NMR experiments were carried out on a Bruker DRX-400 MHz spectrometer (400.13 MHz for proton, 100.61 MHz for carbon, THF, 295 K).

Table 1 Charge distribution and hybridization for the Y skeleton carbons calculated from NMR data.

Position	ρ^a	Hybridization[b]	δ_C	δ_H	$^1J_{CH}$/Hz
Dianion **1**					
1	+0.08	—	145.9	—	—
2	−0.35	2.51	80.4	4.52 s	142.5
Dianion **2**					
1	+0.08	—	146.0	—	—
2	−0.35	2.51	80.5	4.53 s	142.6
2′	−0.35	2.50	80.1	4.51 s	142.7

[a] Charge densities were calculated from the ^{13}C chemical shifts, using O'Brien's equation:[8] $\rho = (\delta_C - 134.1)/153.7$, δ_C expressed in ppm. [b] Carbon hybridization was evaluated from the C–H coupling constants using the equation: $n = 500/^1J_{CH} - 1$, where n is the power in sp^n, $^1J_{CH}$ is expressed in Hz units.

Dianions **1** and **2** were prepared by a double deprotonation using *n*-butyllithium (without TMEDA) from the corresponding olefins. The olefins were prepared by a known procedure[7] ‡ (three isomers exist in the case of [H_2]**2**§). Both dianions **1** and **2** and the starting materials, *i.e.* olefins [H_2]**1** and [H_2]**2** were characterized by NMR spectroscopy.

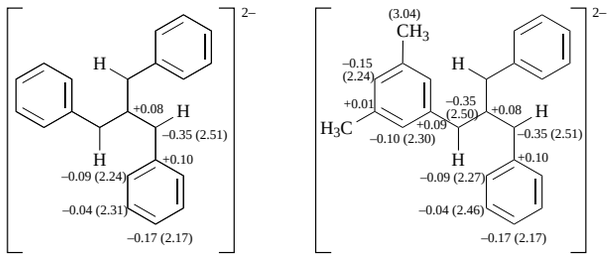
In order to simplify the discussion we shall denote all the 2- and 2′-positions as 'benzylic positions' [and accordingly the 'benzylic bonds' will be all the bonds (C-2)–(C-3) and (C-2′)–(C-3′)], whereas whenever it will be needed to distinguish between the 2- and 2′-positions it will be denoted specifically.

Dynamic NMR experiments on the dianions in the temperature range 185 K–300 K revealed a dynamic behaviour for all the ortho and meta methine sites of **1** [$\Delta G^{\ddagger}_{241.7}$(H-4) = 44.8 ± 1.3 kJ mol^{-1} and $\Delta G^{\ddagger}_{213.6}$(H-5) = 44.8 ± 1.3 kJ mol^{-1}] and **2** [$\Delta G^{\ddagger}_{240.5}$(H-4) = 44.4 ± 1.3 kJ mol^{-1}, $\Delta G^{\ddagger}_{214.0}$(H-5) = 45.2 ± 1.3 kJ mol^{-1} and $\Delta G^{\ddagger}_{236.3}$(H-4′) = 43.5 ± 1.3 kJ mol^{-1}], and also for the two methyl groups of **2** ($\Delta G^{\ddagger}_{214.0}$ = 47.3 ± 4.2 kJ mol^{-1}). This behaviour indicates the freezing of the rotation around the benzylic bonds on the NMR timescale. It is important to point out that the Y-frame protons in both dianions did not reveal any significant dynamic process.¶ Furthermore, C–H coupling constants measured for the benzylic positions indicate a hybridization (Table 1) of approximately $sp^{2.5}$ (in both dianions) as compared with *ca.* sp^2 hybridization for the ring carbons. Similarly, the charge densities (Table 1) at the Y-frame carbons indicate that only *ca.* 50% of the net charge (2−) remained on the Y framework (in both

‡ For the preparation of [H_2]**2** ethyl (3,5-dimethylphenyl)acetate was used.

§ New compounds gave satisfactory mass spectra 2-benzyl-1-(3,5-dimethylphenyl)-3-phenylpropan-2-ol: white crystals, 21% yield, mp: 64 °C. Dehydration afforded three isomers ([H_2]**2**): yellow oil, 80% yield, which were identified in the ^1H NMR spectrum.

¶ The H-2 and H-2′ protons of **2** were shifted at 245.8 K, but remained as singlets, retaining the same integration ratio of 2:1.



1 **2**

Fig. 1 Charge distribution and hybridization (in parentheses) of dianions **1** and **2**

dianions), and it follows that about half the charge was withdrawn from the Y framework (Fig. 1).

All these data lead us to the conclusion that the benzylic bonds in both dianions had become closer in character to double bonds, due to an efficient p-π conjugation and delocalization of the extra charge into the rings. It is still not evident whether the rotation around the Y bonds slowed down with the lowering of the temperature. Slowing down the rotation about the Y bonds would have led to a fixed conformation, that corresponds to the global minimum of the potential energy surface. Bearing in mind that H-2 protons remained isochronous in both dianions **1** and **2** even at the lowest temperature measured, and that the two methyl groups of **2** became non-equivalent upon cooling, one may try to satisfy all the conditions by suggesting a conformation which has the two benzylidene groups in '*exo*,*exo*' or '*endo*,*endo*' positions (but not in '*exo*,*endo*' positions), and the plane of the substituted ring perpendicular to the Y plane. In this conformation the plane of the substituted ring bisects the Y framework and forms a plane of reflection between the two benzylidene groups. Nevertheless, this conformation is not feasible, because placing the substituted ring perpendicular to the Y plane turns its benzyl p-orbital (C-2′) also perpendicular to the other p-orbitals (C-2), thus breaking its conjugation with the rest of the π-system. Such an extreme situation requires that the substituted benzyl group should behave totally differently from the other benzyl groups. The similarity of the $\Delta G^{\ddagger}$ calculated values as well as the even charge distribution negate this option. Another phenomenon to be taken into account is the hybridization of all the benzylic carbons (about $sp^{2.5}$), which implies a strong pyramidalization of these carbons, thus making the two H-2 protons of dianion **2** non-equivalent in any possible conformation. MNDO calculations[6] on **1** and the X-ray structure of **1**–2TMEDA ($2Li^{+}$)[9] show that **1** should exist in a most stable propeller-like conformation (support for this conformation is found in the dynamic behaviour of the methyl groups of **2**). Assuming that **2** does not vary much (as is the case with the other properties), this conformation should distinguish one H-2 proton from the other. Since this has not been found even at the lowest temperature in spite of the hybridization measured, MNDO and X-ray findings, it is inevitable that the rotation about the Y bonds is fast in the NMR timescale.

This reasoning leads us to the conclusion that the Y bonds are weaker than the benzylic bonds.‖ This conclusion supports the notion that Y shaped dianions do not obtain some kind of through-the-center delocalization as a means of stabilization, but they rather tend to distribute the extra charge to the 'corners', thus minimizing the electrostatic repulsions between the three lone pairs. Although we are aware of the steric and electronic effects of the phenyl rings, we believe that the data reported here are experimental support to the theoretical considerations mentioned above, which claim the Coulombic interactions to be the governing factor, and they may also point to the ability of TMM^{2-} and its derivatives to delocalize the extra charge in a most efficient way, which seems to be the origin of the remarkable stability of trimethylenemethane dianion (TMM^{2-}).

‖ The X-ray data of **1**–2TMEDA ($2Li^{+}$)[8] show two Y bonds which are indeed longer than their corresponding benzylic bonds (1.443, 1.460 Å compared to 1.441, 1.434 Å respectively), and a shorter third Y bond.

References

1 J. Klein and A. Medlik, *Chem. Commun.*, 1973, 275.
2 P. Gund, *J. Chem. Educ.*, 1972, **49**, 100.
3 J. Klein, A. Medlik-Balan, A. Y. Meyer and M. Chorev, *Tetrahedron*, 1976, **32**, 1839; J. Klein, *Tetrahedron*, 1983, **39**, 2733; 1988, **44**, 503.
4 K. B. Wiberg, *J. Am. Chem. Soc.*, 1990, **112**, 4177.
5 (*a*) A. Gobbi, P. J. MacDougall and G. Frenking, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1001; (*b*) A. Skancke, *J. Phys. Chem.*, 1994, **98**, 5234, and references cited therein.
6 D. Wilhelm, T. Clark, P. v. R. Schleyer, K. Buckl and G. Boche, *Chem. Ber.*, 1983, **116**, 1669.
7 G. Boche, K. Buckl, D. Martens and D. R. Schneider, *Liebigs Ann. Chem.*, 1980, 1135.
8 H. O'Brien, A. J. Hart and C. R. Russell, *J. Am. Chem. Soc.*, 1975, **97**, 4410.
9 D. Wilhelm, H. Dietrich, T. Clark, W. Mahdi, A. J. Kos and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1984, **106**, 7279.

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