

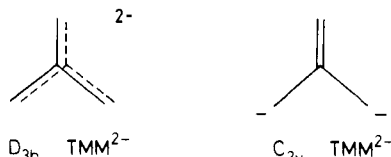
# Trimethylenemethane Dianion and the Controversial Notion of "Y-Aromaticity"

Israel Agranat\*<sup>†</sup> and Anne Skancke\*<sup>‡</sup>

Contribution from the Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel, and the Department of Mathematical and Physical Sciences, University of Tromsø, N-9001 Tromsø, Norway. Received June 28, 1984

**Abstract:** The Y-shaped trimethylenemethane dianion (TMM<sup>2-</sup>) has been studied by RHF ab initio calculations at the 6-31G level. The planar  $D_{3h}$  form was found to be the most stable conformation. The barriers for 1, 2, and 3 rotations were found to be 21.7, 60.6, and 159.4 kcal/mol, respectively. Moreover, the planar  $D_{3h}$  TMM<sup>2-</sup> form was found to be more stable than the isoelectronic, linearly delocalized butadiene dianions by about 30 kcal/mol. The alternation of charges (as calculated on the basis of Mulliken population analysis) was found to be more pronounced than in related systems. The notion of the Y-aromaticity is considered and vitalized on the basis of these data. The unstable character of the triply rotated TMM<sup>2-</sup> was found to be appropriately termed "Möbius antiaromaticity" since the destabilizing delocalization is pericyclic.

The notions of "Y-delocalization" and "Y-aromaticity" were introduced by Gund in 1972 in order to explain the unique properties of guanidine and the guanidinium ion and as a basis for the following prediction: acyclic compounds with closed shell Y-delocalized  $6\pi$ -electron configuration should possess "aromatic" stability.<sup>1</sup> Theoretical interest in the  $6\pi$ -electron system trimethylenemethane dianion (TMM<sup>2-</sup>) and its potential significance was first noted by Finnegan in 1969, who quoted a value of 26 kcal/mol for its resonance energy, ca. 11 kcal/mol more than that of the corresponding monoanion (based presumably on Hückel calculations).<sup>2</sup> The disodium and dipotassium derivatives of TMM<sup>2-</sup> have apparently been prepared previously, although no direct proof of their formation has been given.<sup>3</sup> Klein and Medlik were the first to prepare and characterize TMM<sup>2-</sup> as a dilithium derivative by dimetalation of 2-methylpropene (isobutene) with butyllithium in the presence of tetramethylenediamine (in hexane) and established its structure, providing chemical and spectroscopic (<sup>1</sup>H NMR) evidence for its formation.<sup>4</sup> The dianion adopts a planar, symmetrical delocalized  $D_{3h}$  geometry rather than a  $C_{2v}$  Kekulé structure. They pointed at the exceptional kinetic stability



of TMM<sup>2-</sup> and noted that certain cross-conjugated species such as planar TMM<sup>2-</sup> may possess a novel aromatic character, the so-called "Y-aromaticity".<sup>4,5</sup> Dimetalation of 2-methylpropene proceeded faster than monometalation in spite of the introduction of (part of) the second charge into the same conjugated system and into the same negatively charged peripheral carbon atoms. Later, Klein et al. questioned their initial idea of acyclic Y-aromaticity and the inclusion of the cross-conjugated  $6\pi$ -electron system into the class of aromatics, claiming that this might blur even more the border between aromatics and nonaromatics.<sup>6</sup> However, they argued that the exclusion of the cross-conjugated systems from the group of aromatics did not imply lack of stabilization and resonance, so that TMM<sup>2-</sup> belongs to the large group of resonance-stabilized compounds. Their CNDO calculations supported the interpretation of a planar closed-shell aromatic character of TMM<sup>2-</sup> with equal CC bonds and with all the negative charges equally distributed on the peripheral carbons and some positive charges on the central carbon (a "hole") but indicated a slight repulsive (negative) overlap population between the peripheral methylenes.<sup>6</sup> This seemed to be in contradiction with the hypothesis of through-space delocalization of the  $\pi$ -

electron sextet between the three methylenes, which was supposedly implied by Y-aromaticity. The reliability of the CNDO calculation was later questioned.<sup>7</sup> Klein has recently reviewed in depth the question of Y-aromaticity, Y-delocalization, and cross-conjugation.<sup>7</sup>

Mills has reclaimed the importance of Y-aromaticity of certain cross-conjugated dianions on the basis of the <sup>1</sup>H NMR chemical shift of TMM<sup>2-</sup> ( $\delta$  0.23) (and related species) and its correlation with the  $\pi$ -electron density of aromatic ions.<sup>8</sup> Further studies on the dimetalation of 2-methyl-1,5-hexadiene provided evidence against Y-aromaticity.<sup>9</sup> Although cross-conjugated 2-methylenepentadienyl dianions proved to be more stable than the linear hexatriene dianion, formation of two allylic monoanions was favored over Y-aromatic dianions. Originally, Y-aromaticity was evoked only with compounds possessing  $(4n + 2)$   $\pi$  electrons.<sup>10</sup> A recent study on the dianions derived from 2,5-dimethyl-2,4-hexahexadiene pointed at the stability of an  $8\pi$ -electron cross-conjugated system, a Y-aromatic dianion with  $4n$   $\pi$  electrons.<sup>11</sup> However, this conclusion was qualified: the preference for cross-conjugation may reflect thermodynamic stability which is not due to Y-aromaticity.<sup>11</sup>

Application of the Hess and Schaad method to delocalized dicarbanions gave larger values of resonance energies per atom (REPA) for TMM<sup>2-</sup> and related cross-conjugated dianions, as compared with the corresponding linear dianions and cyclic dianions.<sup>12</sup> According to the REPA criterion, TMM<sup>2-</sup> ( $0.069\beta$ ) is aromatic, the butadiene dianion (BD<sup>2-</sup>) ( $-0.040\beta$ ) is antiaromatic, and the cyclobutadiene dianion (CBD<sup>2-</sup>) ( $-0.001\beta$ ) is nonaromatic. However, the allyl anion (AL<sup>1-</sup>) (REPA =  $0.055\beta$ ) is also thermodynamically highly stabilized. Although REPA (TMM<sup>2-</sup>) - REPA (AL<sup>1-</sup>) =  $0.014\beta$ , in the dimetalation of 2-methylhexadiene, the formation of two isolated allylic monoanions

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\* The Hebrew University of Jerusalem.

<sup>‡</sup> University of Tromsø.

was preferred over the Y-aromatic dianion.<sup>9</sup>

Inagaki and Hirabayashi argued in favor of acyclic aromaticity of  $TMM^{2-}$  (and related species), showing that the extent of its electron delocalization is determined by the orbital-phase continuity-discontinuity properties and estimating the one-electron delocalization energy (OEDE) as  $1.56\beta$  as compared with  $1.33\beta$  for the butadiene dianion ( $BD^{2-}$ ).<sup>13</sup>

Schleyer et al. have compared the calculated heats of formation (MNDO SCF MO) of the following three alternative  $\pi$ -conjugated isomers with common  $\sigma$  skeletons but with different delocalized  $\pi$  systems: linear, Y, or cyclic. The calculations indicated that the Hückel stability predictions do not apply to the highly charged small ring systems. Coulombic repulsion in the four-membered ring dianion (and dication) was more important than Hückel aromaticity and led to a preference of the Y-delocalized isomer with a more favorable  $\pi$  charge distribution.<sup>14</sup> The stereochemistry of 2,3-diphenyltrimethylenemethane indicated a preference for the exo,exo conformation.<sup>15</sup>

In contrast to  $TMM^{2-}$  systems, substituted  $TMM^{2+}$  have not so far shown the expected Y-aromatic stabilization.<sup>16</sup>

Another theoretical approach to analyze the relative stabilities of the three topologically alternative  $C_4$  6 $\pi$ -electron delocalized dianions is Dewar's PMO method as applied for polyanions by Klein.<sup>7</sup> Application of this method to the union of the methyl anion with the allyl anion gave the following qualitative order of stabilities:  $TMM^{2-}$  (Y)  $\geq$  cyclobutadiene dianion ( $CBD^{2-}$ ) (cyclic)  $\geq$  butadiene dianion ( $BD^{2-}$ ) (linear). The stabilization of  $TMM^{2-}$  has also been analyzed in terms of charge alternation.<sup>7</sup>  $TMM^{2-}$  was pictured as an ethylene carrying two donors ( $CH_2^-$  groups) on the same carbon, thus reaching an effective charge alternation. By contrast, the butadiene dianion was pictured as an ethylene carrying two identical donors ( $CH_2^-$  groups) on carbon atoms of different sets (starred and unstarred), resulting in an ineffective charge alternation and thus to a lower degree of stabilization (vide infra).<sup>7</sup> In  $CBD^{2-}$ , charge alternation in the four-membered ring is ruled out altogether.

In view of the pivotal role (double entendre) played by  $TMM^{2-}$  as the archetype cross-conjugated Y-aromatic 6 $\pi$ -electron system, it is surprising that the ab initio MO SCF study of  $TMM^{2-}$  and  $TMM^{2+}$  in contrast to the non-Kekulé hydrocarbon diradical ( $TMM$ )<sup>17</sup> has not been reported. The present article tries to fill this gap, considers the controversial notion of Y-aromaticity, and provides some clues to Möbius antiaromaticity. Recently, an ab initio MO study of the molecular geometries and relative stabilities of planar acyclic  $\pi$ -conjugated  $C_8H_8$  dianions has been described.<sup>18</sup>

One of the most important and yet difficult aspects in evaluating the aromaticity and delocalization of a given conjugated species or conformation is the choice of a proper reference system for comparison.<sup>5,19</sup> In an attempt to evaluate the aromatic character of planar  $TMM^{2-}$ , the following reference systems have been considered: planar Kekulé  $C_{2v}$   $TMM^{2-}$  conformations with optimized or characteristic localized CC bonds,  $TMM^{2-}$  orthogonal conformations, planar *s-cis*-butadiene dianion ((*Z*)- $BD^{2-}$ ), planar *s-trans*-butadiene dianion ((*E*)- $BD^{2-}$ ), *gauche*-butadiene dianion ( $\perp$ - $BD^{2-}$ ), allyl anion ( $AL^{1-}$ ), and planar  $D_{3h}$   $TMM^{2+}$ . Upon successive 90° rotations of the peripheral methylene groups of  $TMM^{2-}$ , the following three conformations are formed: single orthogonal  $TMM^{2-}$  (0°, 0°, and 90°)( $1\perp$ - $TMM^{2-}$ ), double or-

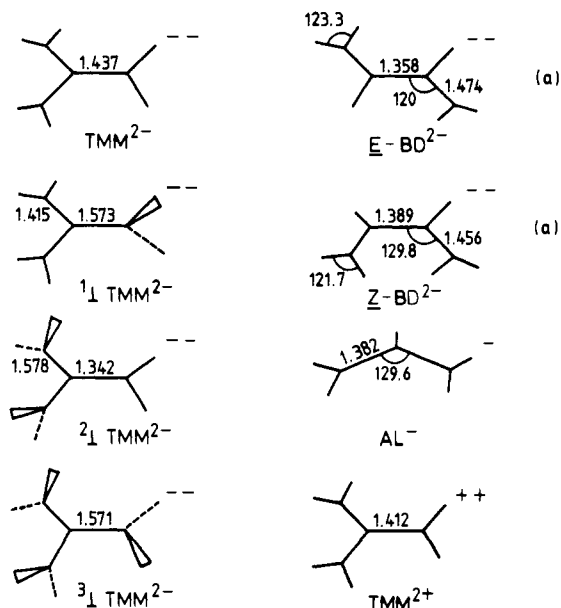


Figure 1. Optimized geometries of  $TMM^{2-}$  and related species at the 6-31G//6-31G level and (a) 4-31G//6-31G level.

Table I. Total 6-31G//6-31G Energies ( $E$ ), Relative Energies ( $\Delta E$ ), and Rotational Energies (RB and  $\Delta RB$ ) of Planar  $D_{3h}$   $TMM^{2-}$  and Related Species

	$E$ , au	$\Delta E$ , kcal/mol	RB, kcal/mol	$\Delta RB$ , kcal/mol
planar $D_{3h}$ $TMM^{2-}$	-154.4995	0.0	0.0	0.0
$1\perp$ - $TMM^{2-}$	-154.4641	21.7	21.7	21.7
$2\perp$ - $TMM^{2-}$	-154.4030	60.6	60.6	38.9
$D_{3h}$ $3\perp$ - $TMM^{2-}$	-154.2458	159.4	159.4	98.6
$C_{2v}$ $3\perp$ - $TMM^{2-}$	-154.2407	162.0	162.0	101.4
planar $D_{3h}$ $TMM^{2+}$	-154.0813			
( <i>Z</i> )- $BD^{2-}$	-154.4574	26.4	0.0	
( <i>E</i> )- $BD^{2-}$	-154.4507	30.6	4.2	
$\perp$ - $BD^{2-}$	-154.3485	94.8	68.4	
planar $AL^{1-}$	-116.3530		0.0	
$1\perp$ - $AL^{1-}$	-116.2981		34.5	
$2\perp$ - $AL^{1-}$	-116.1278		141.4	
planar $C_{2v}$ $TMM^{2-a}$	-154.4814	11.4		
planar relaxed $C_{2v}$ $TMM^{2-}$	-154.4899	6.03		

<sup>a</sup> Kekulé form,  $r_1 = 1.54 \text{ \AA}$ ,  $r_2 = 1.34 \text{ \AA}$ .

thogonal  $TMM^{2-}$  (0°, 90°, and 90°)( $2\perp$ - $TMM^{2-}$ ), and triple orthogonal  $TMM^{2-}$  (90°, 90°, and 90°)( $3\perp$ - $TMM^{2-}$ ).

### Method of Calculation

The calculations have been carried out within the framework of the restricted Hartree-Fock method by using the GAUSSIAN 76 computer program.<sup>20</sup> The optimizations have been carried out by using the 6-31G basis set. Although it is well-known that anionic species pose specific problems in the selection of the basis sets, the choice was justified by the rather limited scope of calculating energy differences between related species where errors are known to cancel to a large extent. It should be pointed out, however, that the computed structure data, charges, and overlaps are not to be considered as "correct" values but rather as a guidance for studying trends within this series of anionic species.

### Results

The optimized geometries of  $TMM^{2-}$  and related species are described in Figure 1. The total ab initio energies and rotational barriers of  $TMM^{2-}$  and related species are given in Table I. The gross atomic charges are given in Table II, and values of charge alternation are given in Table III. Carbon-carbon overlap of  $TMM^{2-}$  and related species are given in Table IV.

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Table II. Gross Atomic Charges of TMM<sup>2-</sup> and Related Species<sup>a</sup>

	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	H <sub>1</sub>	H <sub>2</sub>	H <sub>3</sub>	H <sub>4</sub>	H <sub>5</sub>	H <sub>6</sub>
planar D <sub>3h</sub> TMM <sup>2-</sup>	+0.353	-0.660	-0.660	-0.660	-0.062	-0.062	-0.062	-0.062	-0.062	-0.062
planar C <sub>2v</sub> TMM <sup>2-b</sup>	+0.333	-0.668	-0.668	-0.650	-0.062	-0.070	-0.062	-0.070	-0.043	-0.043
<sup>1</sup> ⊥-TMM <sup>2-</sup>	+0.316	-0.747	-0.605	-0.605	-0.032	-0.032	-0.073	-0.073	-0.074	-0.074
<sup>2</sup> ⊥-TMM <sup>2-</sup>	+0.292	-0.733	-0.733	-0.465	-0.084	-0.084	-0.084	-0.084	-0.013	-0.013
D <sub>3h</sub> <sup>3</sup> ⊥-TMM <sup>2-</sup>	+0.518	-0.762	-0.762	-0.762	-0.039	-0.039	-0.039	-0.039	-0.039	-0.039
planar D <sub>3h</sub> TMM <sup>2+</sup>	-0.227	+0.011	+0.011	+0.011	+0.366	+0.366	+0.366	+0.366	+0.366	+0.366
planar AL <sup>1-</sup>	-0.578	-0.004	-0.578		+0.036	+0.018	+0.049	+0.031	+0.017	
planar C(NH <sub>2</sub> ) <sub>3</sub> <sup>c,d</sup>	+1.141	-0.918	-0.918	-0.918	+0.435	+0.435	+0.435	+0.435	+0.435	+0.435
C <sub>2v</sub> <sup>3</sup> ⊥-TMM <sup>2-</sup>	+0.095	-0.521	-0.521	-0.494	-0.093	+0.093	+0.093	+0.093	-0.094	+0.094

<sup>a</sup>Note the different numbering scheme in TMM species and AL<sup>1-</sup>. <sup>b</sup>Kekulé form, r<sub>1</sub> = 1.54 Å, r<sub>2</sub> = 1.34 Å. <sup>c</sup>In guanidinium cations, the peripheral atoms are nitrogens (N<sub>2</sub>, N<sub>3</sub>, and N<sub>4</sub>). <sup>d</sup>From ref 30a.

Table III. Charge Alternation in TMM<sup>2-</sup> and Related Species

	C <sub>1</sub> -C <sub>j</sub>	Σ(C <sub>1</sub> -C <sub>j</sub> )	C <sub>1</sub> -H <sub>i</sub>	Σ(C <sub>1</sub> -H <sub>i</sub> )	CA
planar D <sub>3h</sub> TMM <sup>2-</sup>	1.013	3.039	0.598	3.588	6.627
planar C <sub>2v</sub> TMM <sup>2-a</sup>	0.995	2.985	0.604	3.622	6.607
planar D <sub>3h</sub> TMM <sup>2+</sup>	0.238	0.714	0.355	2.130	2.844
<sup>1</sup> ⊥-TMM <sup>2-b</sup>	0.921	1.842	0.678	2.714	4.551
planar AL <sup>1-</sup>	0.582	1.164	0.492	2.459	3.623
C(NH <sub>2</sub> ) <sub>3</sub> <sup>1+c,d</sup>	2.059	6.177	1.353	8.118	14.295

<sup>a</sup>Kekulé form, r<sub>1</sub> = 1.54 Å, r<sub>2</sub> = 1.34 Å. <sup>b</sup>Allyl fragment only. <sup>c</sup>The peripheral atoms are nitrogen. <sup>d</sup>From ref 30a.

Table IV. Carbon-Carbon Overlap Populations of TMM<sup>2-</sup> and Related Species

	C <sub>1</sub> -C <sub>2</sub>	C <sub>1</sub> -C <sub>3</sub>	C <sub>1</sub> -C <sub>4</sub>	C <sub>2</sub> -C <sub>3</sub>	C <sub>2</sub> -C <sub>4</sub>	C <sub>3</sub> -C <sub>4</sub>
planar D <sub>3h</sub> TMM <sup>2-</sup>	+1.041	+1.041	+1.041	-0.179	-0.179	-0.179
planar C <sub>2v</sub> TMM <sup>2-a</sup>	+1.004	+1.004	1.072	-0.110	-0.204	-0.204
<sup>1</sup> ⊥-TMM <sup>2-</sup>	+0.652	+1.140	+1.140	-0.142	-0.142	-0.269
<sup>2</sup> ⊥-TMM <sup>2-</sup>	+0.672	+0.672	+1.249	-0.203	-0.184	-0.184
D <sub>3h</sub> <sup>3</sup> ⊥-TMM <sup>2-</sup>	+0.668	+0.668	+0.668	-0.262	-0.262	-0.262
D <sub>3h</sub> planar TMM <sup>2+</sup>	+0.635	+0.635	+0.635	-0.032	-0.032	-0.032
planar AL <sup>1-</sup>	+1.098	-0.190		+1.098		
C <sub>2v</sub> <sup>3</sup> ⊥-TMM <sup>2-</sup>	+0.838	+0.838	+0.865	-0.038	-0.024	-0.024

<sup>a</sup>Kekulé form, r<sub>1</sub> = 1.54 Å, r<sub>2</sub> = 1.34 Å.

## Discussion

**Planar D<sub>3h</sub> TMM<sup>2-</sup>.** The most stable conformer of TMM<sup>2-</sup> in the ground state adopts a planar geometry of D<sub>3h</sub> symmetry (computed energy: -154.4995 au) with equal CC bond lengths of 1.437 Å and normal sp<sup>2</sup> bond angles of 120° (CCC, HCC, and HCH). This Y-delocalized picture contrasts with the pronounced bond alternation in the planar *s-trans*-butadiene dianion ((*E*)-BD<sup>2-</sup>) (C<sub>1</sub>C<sub>2</sub> = 1.358 Å, C<sub>1</sub>C<sub>3</sub> = C<sub>2</sub>C<sub>4</sub> = 1.474 Å, and r<sub>1</sub>-r<sub>2</sub> = 0.116 Å). In the planar *s-cis*-butadiene dianion ((*Z*)-BD<sup>2-</sup>) (C<sub>1</sub>C<sub>2</sub> = 1.400 Å, C<sub>1</sub>C<sub>3</sub> = C<sub>2</sub>C<sub>4</sub> = 1.469 Å, and r<sub>2</sub>-r<sub>1</sub> = 0.069 Å), the effect of bond alternation is smaller, similar to *all-trans*-polyacetylene<sup>21</sup> (r<sub>2</sub>-r<sub>1</sub> = 0.066 Å), while in the *gauche*-butadiene dianion (⊥-BD<sup>2-</sup>) the CC bond lengths are almost equal (C<sub>1</sub>C<sub>2</sub> = 1.451 Å, C<sub>1</sub>C<sub>3</sub> = C<sub>2</sub>C<sub>4</sub> = 1.441 Å, and r<sub>2</sub>-r<sub>1</sub> = 0.010 Å). The CC bond length in planar TMM<sup>2-</sup> lies midway between the CC single bond value (1.54 Å) and the CC double bond value (1.34 Å). It is very close to the average CC bond lengths in the planar *s-trans*- and *s-cis*-butadiene dianions (1.435 and 1.434 Å, respectively) and significantly longer than the CC bond lengths of the planar allyl anion (1.382 Å) and the experimentally determined CC bonds in benzene (1.398 Å) and hexagonal α-graphite (1.415 Å).<sup>21,22</sup>

Recently, a hypothetical metallic allotrope of carbon constructed of a three-dimensional trigonal sp<sup>2</sup> carbon network of infinite polyene chains has been envisaged.<sup>23</sup> The assumed equal nonalternating CC distance of 1.44 Å within these polyenes resembles the computed length of 1.437 Å in TMM<sup>2-</sup>. The computed distance between the peripheral carbon atoms in planar TMM<sup>2-</sup> is 2.489 Å, somewhat shorter than the corresponding distance in

the allyl anion (2.501 Å) but longer than the meta CC distance in graphite (2.451 Å). In view of the planar geometry of TMM<sup>2-</sup>, only pp-π and no pp-σ overlaps are considered.<sup>24</sup>

The most meaningful results in the present investigation are the relative energies of the various C<sub>4</sub>H<sub>6</sub><sup>2-</sup> conformations. The D<sub>3h</sub> form of planar TMM<sup>2-</sup> is more stable than the relaxed C<sub>2v</sub> form by 6.05 kcal/mol. Perhaps more meaningful is the difference between the Y-delocalized ground state and a localized hypothetical C<sub>2v</sub> Kekulé TMM<sup>2-</sup> (r<sub>1</sub> = 1.54 Å, r<sub>2</sub> = 1.34 Å), 11.4 kcal/mol. The difference in stability between the D<sub>3h</sub> and C<sub>2v</sub> forms depends somewhat on the choice of geometry of the latter form. For example, for r<sub>1</sub> = 1.54 Å and r<sub>2</sub> = 1.32 Å, ΔE = 13.4 kcal/mol, for r<sub>1</sub> = 1.51 Å and r<sub>2</sub> = 1.32 Å, ΔE = 10.2 kcal/mol, and for r<sub>1</sub> = 1.518 Å and r<sub>2</sub> = 1.342 Å (computed bond lengths of <sup>2</sup>⊥-TMM<sup>2-</sup>), ΔE = 8.5 kcal/mol.

Planar TMM<sup>2-</sup> is more stable than planar (*E*)-BD<sup>2-</sup> by 30.62 kcal/mol, a striking manifestation of a pronounced Y-delocalization vs. linear delocalization. In planar (*E*)-BD<sup>2-</sup> and (*Z*)-BD<sup>2-</sup>, the CCC angles are 120° and 129.7°, respectively. The former dianion is therefore a more appropriate model for comparison with TMM<sup>2-</sup>. (*Z*)-BD<sup>2-</sup> is more stable than (*E*)-BD<sup>2-</sup> by 4.2 kcal/mol, supporting the notion of 6π-electron U-stabilization.<sup>7,25,26</sup> Previous estimates of the heat of formation (MNDO method) indicates a preference of only 15.2 kcal/mol for a Y over a linear four-membered ring C<sub>5</sub>H<sub>6</sub> dianion isomer.<sup>14</sup>

**Rotational Barriers.** The starting point for a discussion of the computed rotational barriers of TMM<sup>2-</sup> and related species is the rotational barrier of simple ethylenes: 62–65 kcal/mol.<sup>27,28</sup> It

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should be borne in mind that the rotation process disrupts the favorable  $\sigma$  interactions in an all-planar geometry and the rotational barrier reflects the difference in the sum total of the bonding properties of the two conformations and not a pure  $\pi$  effect.<sup>29</sup>

The barriers for single, double, and triple 90° rotations around the CC bonds in planar TMM<sup>2-</sup> are 19.2, 60.7, and 159.4 kcal/mol, respectively, indicating a marked hysteresis effect. An analogous trend has been reported for the conformational behavior of the guanidinium cation.<sup>30</sup>

The single 90° rotation in TMM<sup>2-</sup> leads to <sup>1</sup>⊥-TMM<sup>2-</sup>, a dianion constructed of an allylic unit bonded at the center to an orthogonal methylene. In <sup>1</sup>⊥-TMM<sup>2-</sup>, the symmetry is broken and the  $\pi$ -electron contribution is reduced. A simple interpretation of the first rotational barrier is to consider the VB or HMO representation of delocalized planar TMM<sup>2-</sup>, a symmetrical species with three equal CC bonds, each having one-third  $\pi$ -bond contribution (the Hückel CC bond order is 0.577).<sup>31</sup> The rotational barrier around such a CC double bond would be expected to be one-third of that required for rotation in simple ethylenes. The barrier of 19.2 kcal/mol is consistent with this naive description. (The Hückel resonance energy of planar *D*<sub>3h</sub> TMM<sup>2-</sup> is 1.464 $\beta$ <sup>31</sup> or 47.9 kcal/mol, assuming  $\beta = 32.74$ .)<sup>32</sup> This agreement is to a large extent fortuitous. The barrier of 19.2 kcal/mol predominantly reflects the extra enhanced delocalization energy of planar TMM<sup>2-</sup> relative to planar Al<sup>1-</sup>. The role of the orthogonal "methylene anion" in the stabilization (or destabilization) of <sup>1</sup>⊥-TMM<sup>2-</sup> is probably small. Only the antibonding combination of the orthogonal hydrogens contributes in the right symmetry. The total delocalization energy (DE) of TMM<sup>2-</sup>, including the allylic anion term, is 60 kcal/mol ( $E(^2\perp\text{-TMM}^{2-}) - E(\text{TMM}^{2-})$ ). This value may be compared with the delocalization energy of planar Al<sup>1-</sup>, 35 kcal/mol.<sup>33,34</sup> A more meaningful comparison requires a certain normalization taking into account the number of carbon atoms in each conjugated system<sup>12</sup> (DEPA). For planar Al<sup>1-</sup>, DEPA = 11.5 kcal/mol, while for TMM<sup>2-</sup>, DEPA = 15.3 kcal/mol, an increase of 33%. (A normalization to the number of  $\pi$  electrons gives DEPE (Al<sup>1-</sup>) = 8.63 and DEPE (TMM<sup>2-</sup>) = 10.20 kcal/mol.) The results clearly demonstrate a significant Y-delocalization in planar TMM<sup>2-</sup>. For comparison, recent ab initio calculations gave a value of 23.4 kcal/mol for the total resonance energy of benzene (6-31G\*<sup>19</sup>).

The barriers for single rotations around the central CC bond of (*E*)-BD<sup>2</sup> and (*Z*)-BD<sup>2</sup> are characteristic for simple normal CC double bonds, 64.2 and 68.3 kcal/mol, respectively. The corresponding barriers around the external CC bonds are 2.8 and 10.8 kcal/mol, as expected for the geometries and relative single bond character of these linear dianions. It is true that the barrier for a single CC rotation in planar TMM<sup>2-</sup> is considerably lower (by 12.7 kcal/mol) than in planar Al<sup>1-</sup>. Moreover, it is 18.6 kcal/mol lower than the allylic anion rotational barrier in the <sup>1</sup>⊥-TMM<sup>2-</sup> → <sup>2</sup>⊥-TMM<sup>2-</sup> transformation. However, these differences should not be interpreted in terms of relative DE's and do not signify a smaller DE of planar TMM<sup>2-</sup> compared with Al<sup>1-</sup>. Consider the transformation <sup>2</sup>⊥-TMM<sup>2-</sup> → <sup>1</sup>⊥-TMM<sup>2-</sup> → planar TMM<sup>2-</sup> as two consecutive contributors to allylic anion stabilization. The average value of 31.1 kcal/mol is 3.4 kcal/mol smaller than the allylic stabilization energy of 34.5 kcal/mol. The deviation from

additivity in the allyl anion delocalization energy is TMM<sup>2-</sup> is ca. 10%.

Some insight may be gained by comparing the allylic anion component of <sup>1</sup>⊥-TMM<sup>2-</sup> with the parent allyl anion (Al<sup>1-</sup>). The CC rotational barrier is 5.9 kcal/mol higher than the former, although the CC bonds in the parent anion are shorter by 0.033 Å. This indicates a reduced  $\pi$ -bond character in <sup>1</sup>⊥-TMM<sup>2-</sup>. The CCC angles in the two species vary considerably, 120.0° vs. 129.6°. The gross charges on both the external and the central carbons also differ: -0.605 and +0.316 in <sup>1</sup>⊥-TMM<sup>2-</sup> and -0.578 and +0.004 in Al<sup>1-</sup> (vide infra). Charge alternation is therefore more pronounced in the former species. It seems that the conditions for an effective allylic anion delocalization are more favorable in <sup>1</sup>⊥-TMM<sup>2-</sup> than in the parent anion.

It is interesting to compare the two isomeric <sup>2</sup>⊥-TMM<sup>2-</sup> and ⊥-BD<sup>2-</sup> species. Both species may be viewed as an ethylene substituted by two orthogonal CH<sub>2</sub><sup>-</sup> donor groups. However, <sup>2</sup>⊥-TMM<sup>2-</sup> is a gem-distributed ethylene while ⊥-BD<sup>2-</sup> is a vic-disubstituted ethylene. Their total energies differ by only 1.4 kcal/mol, and the charge alternation on the ethylene component is also very similar (0.757 vs. 0.714) and quite small. Thus, the difference in the relative arrangements of the two donor substituents around the ethylene unit does not affect the stabilization of the two "structural" isomeric dianions. This is probably due to the orthogonality of the donors vs. the ethylene unit, which reduces the donor-acceptor interactions.

**Charge Alternation.** Klein has emphasized the importance of charge alternation and donor-acceptor interactions in stabilizing delocalized systems including polyions.<sup>7</sup> A conjugated system containing atoms of different electronegativities or charges reaches its highest stabilization when the number of donor-acceptor interactions is the largest possible.<sup>7</sup> This can be obtained by alternating partial charges on neighboring atoms. Two substituents of the same type (donors or acceptors) are stabilized in a delocalized system when they are placed all on the starred set of atoms in a molecule. Two substituents of different kinds are stabilized when one is on a starred and the other is on an unstarred atom of the molecule. Methylene carrying positive or negative charges are considered acceptors and donors, respectively.<sup>7</sup> The gross charge populations of the conformations of TMM<sup>2-</sup> and related species are given in Table II. An index of charge alternation CA in a planar conjugated system may be defined as the sum of differences of gross charge populations in neighboring atoms *i* and *j*:

$$CA = \sum_{ij} |q_{ii} - q_{jj}|$$

This sum may be divided into two contributions: the interbackbone atoms and the hydrogen-backbone atoms contributions. The values of CA are summarized in Table III. It is evident that the total charge alternation in planar *D*<sub>3h</sub> TMM<sup>2-</sup> (6.627) as well as its backbone (carbon-carbon) contribution (3.039) markedly exceeds the corresponding values in Al<sup>1-</sup>, (*Z*)-BD<sup>2-</sup>, (*E*)-BD<sup>2-</sup>, planar *D*<sub>3h</sub> TMM<sup>2-</sup>, and the allyl anion component of <sup>1</sup>⊥-TMM<sup>2-</sup>. (The CA values may be normalized, e.g., to the number of neighboring alternations.) It may be noted that charge alternations in planar *D*<sub>3h</sub> and *C*<sub>2v</sub> (Kekulé) TMM<sup>2-</sup> hardly differ. In both species a substantial positive charge resides in the center. On the other hand, charge alternation in the guanidinium cation is much more effective than either planar TMM<sup>2-</sup> species.<sup>30</sup>

**Resonance vs. Charge Alternation.** Is cross-conjugation a resonance effect? Klein answered in the negative, maintaining that resonance considerations require that cross-conjugation in polyanions shall be destabilizing.<sup>7</sup> According to Klein, the reason for the enhanced stabilization of cross-conjugated polyions relative to their isomers is not resonance but charge alternation.<sup>7</sup> The arguments against the role of resonance in cross-conjugation are hardly convincing. Consider the case of the three isomeric xylene dianions C<sub>8</sub>H<sub>8</sub><sup>2-</sup> (benzoquinodimethane dianions). Simple resonance considerations predict the following order of stability: 1,3-BQM<sup>2-</sup> > 1,2-BQM > 1,4-BQM<sup>2-</sup>. The same trend is predicted by HMO calculations which give the following values for

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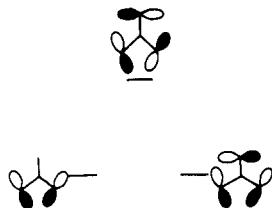


Figure 2.  $\pi$ -Molecular orbitals in  $^3\perp$ -TMM $^{2-}$ .

$\pi$ -delocalization energies:  $3.431\beta$  (1,3-BQM $^{2-}$ ),  $3.364\beta$  (1,2-BQM $^{2-}$ ), and  $3.303\beta$  (1,4-BQM $^{2-}$ ).<sup>31,35</sup> The REPA values are  $0.077\beta$  (1,3-BQM $^{2-}$ ),  $0.065\beta$  (1,2-BQM $^{2-}$ ), and  $0.061\beta$  (1,4-BQM $^{2-}$ ).<sup>12</sup> The experimental evidence supports these predictions.<sup>7,12</sup> Charge alternation in the *m*-xylene dianion (1,3-BQM $^{2-}$ ), which may be viewed as an extended vinologue of TMM $^{2-}$ ,<sup>7</sup> is undoubtedly a resonance effect. In general, charge alternation and resonance are woven together. The importance of resonance in certain organic species, e.g., allylic species, has recently been challenged.<sup>29,36</sup> It has been argued that in many cases  $\pi$  delocalization may be a consequence of the symmetric geometry that is enforced on the  $\sigma$  framework rather than being the driving force for achieving this symmetric geometry.<sup>29</sup>

$^3\perp$ -TMM $^{2-}$ .  $^3\perp$ -TMM $^{2-}$  ("twist-TMM $^{2-}$ ") is formed by three 90° rotations of the methylene groups of planar TMM $^{2-}$ . The peripheral  $\pi$  molecular orbitals of  $D_{3h}$   $^3\perp$ -TMM $^{2-}$  are depicted in Figure 2.  $^3\perp$ -TMM $^{2-}$  is a Möbius system<sup>6,37</sup> (with one or three phase dislocations) predicted to be antiaromatic. Indeed, the calculated barrier for rotation around the CC double bond in  $^2\perp$ -TMM $^{2-}$  leading to  $D_{3h}$   $^3\perp$ -TMM $^{2-}$  is extremely high, 98.8 kcal/mol. This value exceeds by ca. 50% the free energy rotational barriers in simple ethylenes<sup>27</sup> (62–65 kcal/mol), indicating an unusual degree of destabilization in  $D_{3h}$   $^3\perp$ -TMM $^{2-}$ . The relaxed  $C_{2v}$   $^3\perp$ -TMM $^{2-}$  is less stable by 2.6 kcal/mol.

The p orbitals of the peripheral carbons in the elusive  $^3\perp$   $D_{3h}$  TMM $^{2-}$  species are orthogonal to the p orbital of the central carbon but are canted toward each other at an angle of 60°. The CC bond lengths are 1.511 Å (as compared with 1.443 and 1.402 Å in the corresponding  $C_{2v}$  form) and the peripheral CC distances are 2.617 Å. Thus, a significant pp- $\sigma$  overlap of the canted orbitals is expected.<sup>24</sup> (The peripheral distance between the polyene chain of the previously mentioned hypothetical metallic allotrope of carbon is 2.494 Å, far from comfortable for  $\pi$  systems imparting on each other.)<sup>23</sup> This is borne out by the negative CC overlap population of the peripheral carbons in triply rotated  $D_{3h}$  TMM $^{2-}$ , -0.262 (total: -0.668), as compared with -0.179 in planar  $D_{3h}$  TMM $^{2-}$  and -0.190 in planar AL $^{1-}$ . By contrast, the CC peripheral negative overlap population in  $C_{2v}$   $^3\perp$ -TMM $^{2-}$  is negligible (-0.024 and -0.038) in spite of the shortened CC distances ( $C_2C_3 = 2.499$  Å,  $C_2C_4 = C_3C_4 = 2.464$  Å).

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The high repulsive  $C_3C_4$  overlap population of -0.269 in the planar allylic component of  $^1\perp$ -TMM $^{2-}$  deserves a comment. In this species, the allylic  $C_1C_3$  and  $C_1C_4$  bond lengths are 1.415 Å, the CCC angle is 120°, and the  $C_3C_4$  distance is 2.415 Å, shorter by 0.05 Å than in the parent allyl anion. The relative proximity of  $C_3$  and  $C_4$  in  $^1\perp$ -TMM $^{2-}$  as well as their largest gross atomic charges (as compared with the parent allyl anion) may cause the more effective  $C_3C_4$  repulsion. It should be emphasized that the notion of Möbius antiaromaticity in the  $D_{3h}$   $^3\perp$ -TMM $^{2-}$  should not be considered Y-antiaromaticity. Although  $D_{3h}$   $^3\perp$ -TMM $^{2-}$  is a TMM species and as such of Y-topology, the destabilizing delocalization is pericyclic, due to the cyclic array of peripheral canted p orbitals and is not cross-conjugated through the center. A hyperconjugation effect due to the antibonding combination of the three pairs of orthogonal hydrogens and the central p orbital may also play a role.

**Conclusion.** The analysis of the results of the ab initio calculations of TMM $^{2-}$  and related systems outlined in the present study leads to the inevitable unequivocal conclusion: planar  $D_{3h}$  TMM $^{2-}$ , the archetype cross-conjugated 6 $\pi$ -electron Y-shaped system, is distinguished by a novel enhanced stabilization and charge alternation. This thermodynamic effect is a manifestation of acyclic Y-aromaticity par excellence. Y-Aromaticity, just as aromaticity, is a theoretical notion.<sup>38</sup> Aromaticity need not be associated with cyclic topology. It may span over topologies of various dimensions.<sup>39,40</sup> The previous hypothesis<sup>7</sup> of a through-space delocalization of the  $\pi$ -electron sextet among three methylenes in planar  $D_{3h}$  TMM $^{2-}$  should not be a necessary condition for Y-aromaticity. On the contrary, the whole essence of Y-aromaticity is delocalization through the center and not through the periphery. TMM $^{2-}$  is Y-aromatic in spite of the repulsive interactions between its peripheral carbons. Acyclic Y-aromaticity does not preclude cyclic orbital interaction. Indeed, the orbitals in the cyclic array in planar TMM $^{2-}$  (but not in BD $^{2-}$ ) meet the orbital-phase continuity-discontinuity requirements for aromaticity.<sup>13,41</sup>

Some consideration may be given to the effect of  $\sigma$  conjugation due to nonvanishing resonance integrals ( $sp^2-sp^2$ ) on the central carbon atom in TMM $^{2-}$  and related species of Y-topology.<sup>42</sup>

Finally, it is amusing to note the analogy between TMM species and the Steiner problem.<sup>43,44</sup> The carbon  $\sigma$  framework of planar TMM $^{2-}$  is a Steiner minimal tree (the minimum path which joins the three peripheral carbons). The central atom, the junction, is the corresponding Steiner point, which has three lines meeting at exactly 120°. Moreover, the whole  $\sigma$  framework of the dianion, including the C-H bonds, is a Steiner minimal tree, with all four carbon atoms serving as Steiner points.

**Registry No.** TMM $^{2-}$ , 41792-83-0; BD $^{2-}$ , 42206-06-4; AL $^{1-}$ , 1724-46-5.

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