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Structural Consequences of π-Donation by NR$_2$ Groups: Ab Initio Study of Tetrakis(dimethylamino)ethylene (TDAE) and Its Unsubstituted Analog

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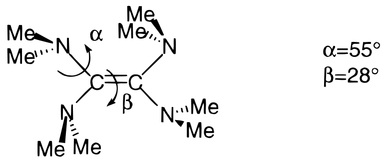
Ab initio calculations have been performed on unsubstituted $(H_2N)_2C{=}C(NH_2)_2$ and methylated $(Me_2N)_2C{=}C(NMe_2)_2$ tetrakis(amino)ethylene. In the unsubstituted system, idealized geometries have been optimized first. Geometrical relaxations by pyramidalization or rotation of the amino groups have been carefully studied. Full geometry optimization leads to a Y-shaped lowest energy structure. Optimized geometry resulting from a synchronous rotation of the amino groups is located 8.1 (HF level) and 6.7 (MP2 level) kcal/mol above in energy. In methylated species where strong steric effects are at work, only two minima are found. Their energy difference is small (1.0 (HF level) and 0.6 kcal/mol (MP2/HF level)). The most stable isomer is Y-shaped, while the secondary minimum exhibits an almost conrotatory motion of the amino groups. This latter minimum is geometrically very close to the experimentally observed molecule. It is concluded that (i) from an electronic point of view, Y-shaped geometry is preferred and (ii) steric effects disfavor this geometry, which becomes energetically competitive with that obtained from a conrotatory motion of the amino groups. It is finally suggested that the existence of two minima close in energy should be at the origin of the phase transitions that are experimentally observed in this material.

Introduction

In unsaturated hydrocarbon, replacement of hydrogen atoms by π-donor substituents such as NR$_2$ groups may lead to substantial changes in chemical properties. For instance, the oxidation potential of *p*-benzoquinone is dramatically lowered by 2.6 V (from 2.85 to 0.25 V) when dimethylamino groups replace the hydrogens of the aromatic ring.[1] Another example is the low reactivity of the guanidium ion ($C(NMe_2)_3{}^+$), which does not react with water despite its electronic deficiency.[2]

Geometrical changes may also occur between unsubstituted and substituted systems. If we restrict ourselves to the interaction between nitrogen lone pairs and the π-system of the unsaturated moiety, two limiting cases can be found. In the first case, the lone pairs of the NR$_2$ groups conjugate with the π-system of the unsaturated skeleton. Such a conjugation is found in guanidium ion.[2] The resulting π-donation from the amino groups toward the cationic carbon may be at the origin of the diminished reactivity of this carbocation. On the contrary, in hexakis(dimethylamino)benzene, the six nitrogen lone pairs are fully deconjugated with respect to the benzene ring.[3] Pyramidalization of the amino substituents is then observed. An intermediate situation is found in tetrakis(dimethylamino)ethylene (TDAE): according to the gas-phase structural determination by Bock et al.,[4] the four amino groups partially deconjugate. A $\alpha = 55°$ rotation of the planes of these groups is observed with respect to the fully conjugated situation. The relative motion of the amino groups is conrotatory. In addition, the two $(Me_2N)_2C$ halves partially deconjugate, the twist angle (β) between them being equal to 28° (**1**). X-ray analysis is in accordance with the gas-phase results.



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More recently, an X-ray diffraction study of TDAE at different temperatures confirms the prominent features of this structure.[5] The twist angle of the C═C bond found to be equal to 28.2° at 218 K[4] slightly reduces to 24.5° at 90 K.[5] From the collected data, we have calculated the mean NMe$_2$ rotation angle to be equal to 49.9° (90 K). In this study, it is also shown that other geometrical parameter values depend on temperature: for instance, C═C bond length increases from 1.348 Å (218 K) to 1.362 Å (90 K) with decreasing temperature. Finally, a careful study of this material indicates that three transition phases occur upon heating at 183, 193, and 242 K.

Theoretical calculations have been previously performed on TDAE as well as on unsubstituted tetrakis(amino)ethylene (TAE).[4,6] Geometrical optimization of TDAE with the AM1 method lead to a planar $N_2C{=}CN_2$ skeleton,[4] the nitrogen lone pairs being fully deconjugated. This result is clearly at odd with the experimental data and may originate from semiempirical methods deficiencies. Ab initio calculations on unsubstituted TAE molecule[6] also lead to a rather surprising result: in the lowest energy structure (optimized at the HF/3-21G level), two amino groups on the same carbon conjugate with the C═C double bond whereas the two other amino groups deconjugate.

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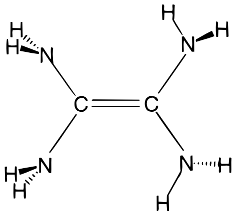
This Y-shaped geometry (**2**) given by these calculations also clearly differ from the observed geometry.



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The available data on TDAE and TAE may be summarized as follows: experimentally, a partial deconjugation of the amino groups from the CC bond occurs through a conrotatory motion. Ab initio calculations do not reflect this feature and give an optimal Y-shaped structure for TAE. We therefore decided to undertake ab initio calculations on both TAE and TDAE in order to understand (i) the electronic preference of the π-system in such molecules and (ii) the role of steric effects at work in TDAE.

Method of Calculation

The 6-31G* basis set was used throughout the paper.[7] For unsubstituted system (TAE), a detailed study of the potential energy surface has been made at the HF level. All stationary points have been optimized with the help of an analytical gradient method (Berny algorithm[8]). Characterizations of the extrema were made by analytical frequency calculations at this level. The stationary points may be minimum (Min, no imaginary frequency) or transition state (TS, only one imaginary frequency) or n-order saddle point (n-SP, n imaginary frequencies). In this last case ($n > 1$), the stationary point has no chemical significance. The located extrema have been reoptimized at the MP2 level. Starting from the minima found for TAE, the methyl groups have been introduced, and the resulting substituted structures have been reoptimized at the HF level. Since calculations on such systems need much computational time, only single-point calculations have been made at the MP2 level on the HF-optimized geometries. The Gaussian 94[8] set of programs was used throughout.

Results

A. Unsubstituted System $C_2(NH_2)_4$. The potential energy surface (PES) of the unsubstituted molecule has been extensively studied at the HF level. Starting from five idealized geometries, two geometrical relaxations (rotation and pyramidalization of the amino groups) have been analyzed. Full geometry optimizations have then been performed on the most important structures. Finally, idealized structures and minima located at the HF level have been reoptimized at the MP2 level.

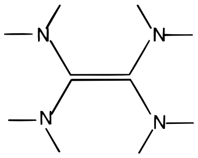
Idealized Geometries. We have first optimized the five idealized structures depicted in **3**−**7**. In **3**, the whole molecule is planar and the four amino substituents conjugate with the π_{CC}-moiety. In **4**, all the NH_2 groups have been rotated by 90° and all of them are fully deconjugated. When only two amino groups conjugate with π_{CC} (the two remaining ones being fully deconjugated), one obtains three structures depending on the relative position of the conjugating groups:[9] in **5** they are located on the same carbon, while they substitute different carbon atoms in cis and trans positions in **6** and **7** respectively.

Structure **5** is an idealization of the Y-structure obtained by Frenking,[6] while **6** and **7** are butadiene-like (cis and trans) structures. All the structures **3**−**7** have been optimized, the amino groups and the C_2N_4 skeleton being kept planar. The results are given in Table 1.

TABLE 1: Main Bond Lengths (in Å) and Relative Energies (Δ*E*, in kcal/mol) of the Five Idealized Structures 3−7 (HF Level). CN_{conj} and CN_{deconj} Are the CN Bond Lengths of Conjugated and Deconjugated Amino Groups, Respectively

structure	C=C	CN_{conj}	CN_{deconj}	Δ*E*
3	1.322	1.406		0[a]
4	1.337		1.410	+5.4
5	1.347	1.369	1.411	−19.2
6	1.332	1.402	1.399	−8.9
7	1.329	1.397	1.405	−13.3

[a] Absolute energy: −298.089 69 au.



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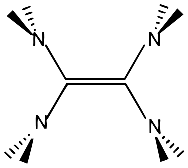

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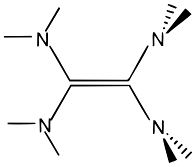

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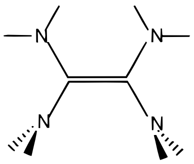

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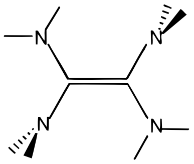

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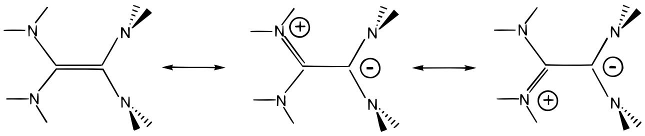
Arbitrarily, the energy of the conjugated structure **3** has been taken as the origin of the energies. This structure is more stable by 5.4 kcal/mol than the fully deconjugated **4**. This may come from a stabilizing conjugation in the π-system and/or different nitrogen lone pair repulsions in the two geometries. However, both these geometries are noticeably higher in energy than those in which only two amino groups conjugate. Among them, the Y-shaped structure **3** is found to be the most stable, in accordance with Frenking's calculations.[6] This result may be related to the so-called Y-aromaticity: an aromatic stabilization may occur when six electrons are shared in four π-orbitals located at the tops and the center of a regular triangle. The relevance of the Y-aromaticity is still under debate.[2,10]

From a geometrical point of view, the main geometrical parameters are quite similar in all structures (Table 1) except in **5**: C−C bond length varies from 1.32 to 1.34 Å and C−N distance from 1.40 to 1.41 Å, whether the amino group is conjugated or not. In Y-shaped structure **5**, the C−C bond length (1.35 Å) is elongated with respect to the preceding structures while the C−N conjugated bonds are shortened (1.37 Å). These differences may be interpreted as resulting from the intervention of the resonating structures depicted in Scheme 1.

Frequency calculations show that none of these idealized structures are minima on the PES: at least four imaginary frequencies are found in each case. Geometrical relaxations of these different structures have then been studied. First, a

SCHEME 1



SCHEME 2

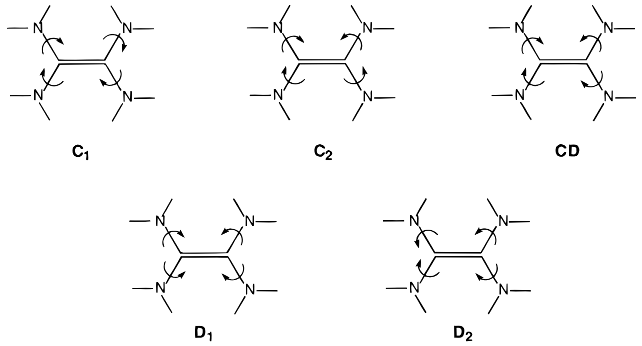


TABLE 2: Rotation Angles (α, in deg) and Stabilization Energies (Δ*E*, in kcal/mol, with Respect to Idealized Structure 3) for the Minimum of Each Coupled Rotation

	C_1	C_2	CD	D_1	D_2
α	40.1	41.7	40.1	36.7	39.3
ΔE	−13.4	−13.6	−9.4	−2.6	−8.9

rotation of the amino groups should reduce the amino lone pair repulsions as previously shown in trivalent BD_3 boron systems with three π-donating groups.[11] Similar deformation is that actually observed in the experimental structure. Second, pyramidalizations of the amino groups that also lead to a stabilization of the molecule have been studied. These two kinds of structural relaxation will be separately analyzed in the following.

Rotation of the Amino Groups. For the sake of simplicity, we will only present the results on coupled rotations of the four amino groups, each of them being kept planar. In each case the interconversion **3** → **4** has been computed. For each $C(NH_2)_2$ moiety, disrotatory and conrotatory motions of the amino groups may occur. Coupling these different motions of each $C(NH_2)_2$ group leads to five different coupled rotations as depicted in Scheme 2.

In $\mathbf{C_1}$ motion, all the amino groups are rotating in a conrotatory manner; similarly, all motions are disrotatory in $\mathbf{D_1}$. For each motion, we have find a stabilization Δ*E* with respect to **3** for a rotation angle α in the range 36−42° (α being equal to zero in **3**). The results are given in Table 2.

Two motions ($\mathbf{C_1}$ and $\mathbf{C_2}$) are stabilizing by about −13.5 kcal/mol whereas $\mathbf{D_1}$ motion is almost nonstabilizing (Table 2), the two other motions leading to intermediate stabilizations. These results may be understood by considering the lone pair repulsion between the amino groups. The interaction of the four NH_2 lone pairs is an eight-electrons/four-OM destabilization, which is analogous to the well-known four-electrons/two-OM repulsion found in He_2. From a monoelectronic point of view, this repulsion only depends on the overlap between the lone pairs. In a conrotatory motion, the overlap between two lone pairs on the same $C(NH_2)_2$ moiety cancels for a rotation angle near 40°.[11] As a consequence, the amino lone pair repulsion becomes negligible for that rotation angle, which is well-reflected by the optimum α angle value found for the two motions $\mathbf{C_1}$ and $\mathbf{C_2}$ (Table 2). On the contrary, the overlap between the amino lone pairs never cancels along a disrotatory motion, and a weak stabilization is found in $\mathbf{D_1}$ motion. This point has been previously analyzed in more detail elsewhere.[11]

SCHEME 3

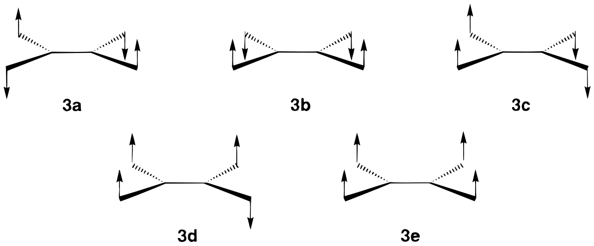


TABLE 3: Range of Pyramidalization Angles (*θ*, in deg) and Stabilization Energies (Δ*E*, in kcal/mol, with Respect to Idealized Structure 3) for Each Pair Isomer

	3a	3b	3c	3d	3e
Δ*E*	−26.4	−21.6	−21.5	−21.3	−14.7
θ	125.0	127.3	127.0	124.4−130.6	130.8

Pyramidalization of the Amino Groups. Starting from the five idealized geometries **3**−**7**, different pyramidalization motions may occur depending on the relative orientation of the hybridized lone pairs. For instance, structure **3** leads to five pair isomers (**3a**−**3e**) as depicted in Scheme 3, in which the arrows symbolize the directions of the hybridized lone pairs. In the optimization process, the C_2N_4 framework has been kept planar and each amino group pyramidalization angle is independently optimized. The relative energies of the five isomers **3a**−**3e** are given in Table 3 with the range of the pyramidalization angles, θ, defined as the angles between the CN bonds and the bisectors of the H−N−H angle. (Note that, for symmetry reasons, only one value of θ is found for **3a**−**3c** and **3e** pair isomers.)

As expected, the largest stabilization is found when the lone pairs may expand in different directions. This is the case in **3a** where all the hybridized adjacent lone pairs develop in trans position with respect to each other. In the same way, the smallest stabilization is found in **3e** where the lone pairs are all cis. Intermediate values are found for the other pair isomers. It should be noted here that the largest stabilization upon pyramidalization (−26.4 kcal/mol in **3a**) is roughly four times the pyramidalization energy in ammonia (6.5 kcal/mol at our level of calculation and 5.8 kcal/mol[12] experimentally observed).

Similar partial optimizations have been performed for idealized structures **4**−**7**. Six pair isomers are found in each case (except in **4** for which seven pair isomers may exist). The definitions of the various isomers are given in Scheme 4, and the energetical results are given in Table 4.

The results in Table 4 show that, as found in structures **3a**−**3e**, the largest stabilization upon pyramidalization occurs when the lone pairs expand in different regions in order to avoid each other. The largest stabilization (−30.2 kcal/mol) is found in structure **4a** in which no conjugation between amino lone pairs and the π_{CC}-system is possible. The stabilization is more than four times the stabilization found in ammonia upon pyramidalization (−26.0 kcal/mol), probably because the amino lone pair repulsion is weaker in pyramidalized structure **4a**. On the contrary, the stabilization is found to be smaller than 26.0 kcal/mol in structures **5**−**7**. We attribute this result to a partial loss of stabilizing conjugation in these structures.

Full Optimization. Starting from the 35 structures precedingly obtained (**C1**, **C2**...**D2**, **3a**...**7f**), a full geometry optimization has been performed at the HF level without any geometrical constraint. Since different structures may collapse on the same

SCHEME 4

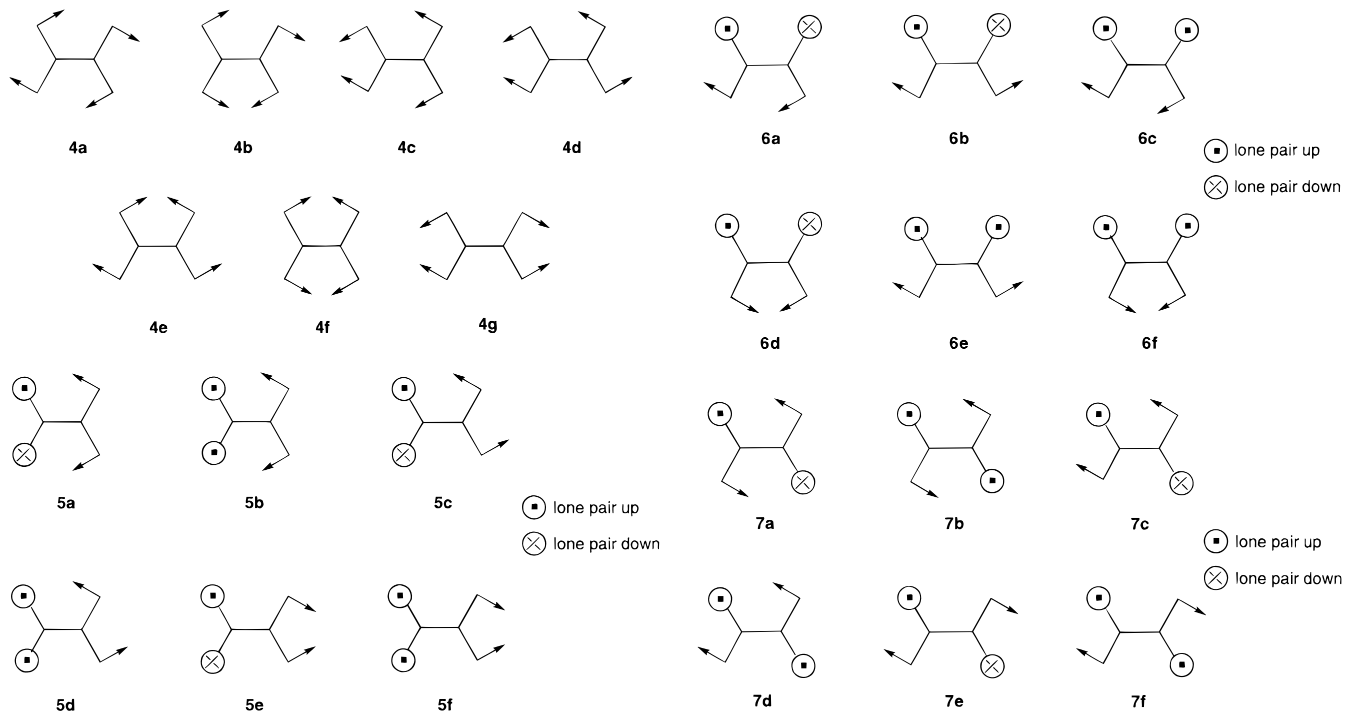


TABLE 4: Mean Pyramidalization Angles (*θ*, in deg) and Stabilization Energies (Δ*E*, in kcal/mol) for Each Pair Isomer

	4a	4b	4c	4d	4e	4f	4g
ΔE	−30.2	−24.9	−24.1	−22.9	−22.6	−20.1	−16.7
θ	122.8	124.0	125.8	126.0	125.3	125.6	129.4

	5a	5b	5c	5d	5e	5f
ΔE	−15.8	−13.6	−12.6	−10.3	−5.3	−2.9
θ	131.7	134.9	129.3	132.7	133.9	136.7

	6a	6b	6c	6d	6e	6f
ΔE	−18.9	−17.0	−16.2	−14.6	−14.3	−11.6
θ	127.6	129.8	129.8	128.3	131.8	130.3

	7a	7b	7c	7d	7e	7f
ΔE	−16.0	−15.6	−13.9	−13.5	−12.5	−12.1
θ	129.5	129.7	131.6	131.4	130.9	131.0

extremum, only 12 different stationary points have been found on the PES. Frequency calculations show that there are eight minima, three transition states, and one second-order saddle point. For the transition states, the imaginary frequency is essentially associated with the rotations of amino groups around C−N bonds. These transition states therefore allow the interconversion between pair isomers. In the following, we will focus on minima. The eight minima (**8**−**15**, Figure 1, Table 5) found on the PES may be described as: (i) three pair isomers of the Y-shaped structure, (ii) three pair isomers of the trans structure and (iii) two minima resulting from the **C$_1$** and **C$_2$** motions. The α rotation angles given in Figure 1 refer to the idealized structures. For instance in **8**, a 3.9° rotation has occurred with respect to a perpendicular geometry of both HN_1H groups. In **C1** and **C2** structures, the rotation angles are given with respect to the fully conjugated geometry. The relative energies are given in Table 5. As previously found by Frenking, the lowest energy structure is Y-shaped and the **C$_1$** structure (rather close to the experimental geometry) is located 8.1 kcal/mol above in energy.

TABLE 5: Main Bond Lengths (in Å), Mean Pyramidalization Angles (*θ*, in deg), and Relative Energies (Δ*E*, in kcal/mol) of the Eight Optimized Structures 8−15 at the HF Level

	8	9	10	11	12	13	14	15
looks like	**5a**	**5b**	**5c**	**7a**	**7f**	**C1**	**C2**	**7e**
ΔE	0^a	3.1	3.8	4.2	5.0	8.1	9.1	9.4
C=C	1.334	1.336	1.332	1.325	1.325	1.328	1.326	1.326
CN_1^b	1.429	1.429	1.430/ 1.429^c	1.422	1.424	1.413	1.415	1.417
CN_2^b	1.391	1.390	1.398/ 1.395^c	1.413	1.413		1.416	1.417
θ_1^b	129.1	129.3	131.5	126.8	128.4	123.9	136.7	134.6
θ_2^b	130.9	134.5	130.7	127.6	125.7		127.2	128.3

[a] Absolute energy: −298.150 74 au, which corresponds to a stabilization of −38.3 kcal/mol with respect to **3**. [b] See Figure 1 for the definition of N_1, N_2 atoms. θ_1, θ_2 refer to pyramidalization angles of N_1 and N_2 atoms, respectively. [c] These two values correspond to the N_1 (N_2) and N_1' (N_2') atoms, see Figure 1.

MP2 Calculations. The five idealized structures **3**−**7** have been reoptimized at the MP2 level, and the results are given in Table 6. The energetical order is the same as that found at the HF level; the relative stability decreases in the order: **5** > **7** > **6** > **3** > **4**. In addition, the relative energies are found to be very close at both levels of calculation, the largest difference (less than 3 kcal/mol) being found for **7** (Table 6). As expected, the optimized bond length values increase from HF to MP2 optimizations (compare Tables 6 and 1). For instance, the CC distance in the lowest energy structure **5** (1.347 Å, HF level) increases to 1.368 Å (MP2 level).

Reoptimization of the eight minima **8**−**15** at the MP2 level leads to only seven different minima (structures **10** and **15** collapse to the same extremum). Basically, the results are the same as those found at the HF level: the same energy ordering is found except for **11**, which becomes the second lowest energy structure (Table 7). The three pair isomers of the Y-shaped structure (**8**, **9**, and **10**) are within 3.5 kcal/mol, and the two pair isomers (**11** and **12**) of the trans structure are located 3.1

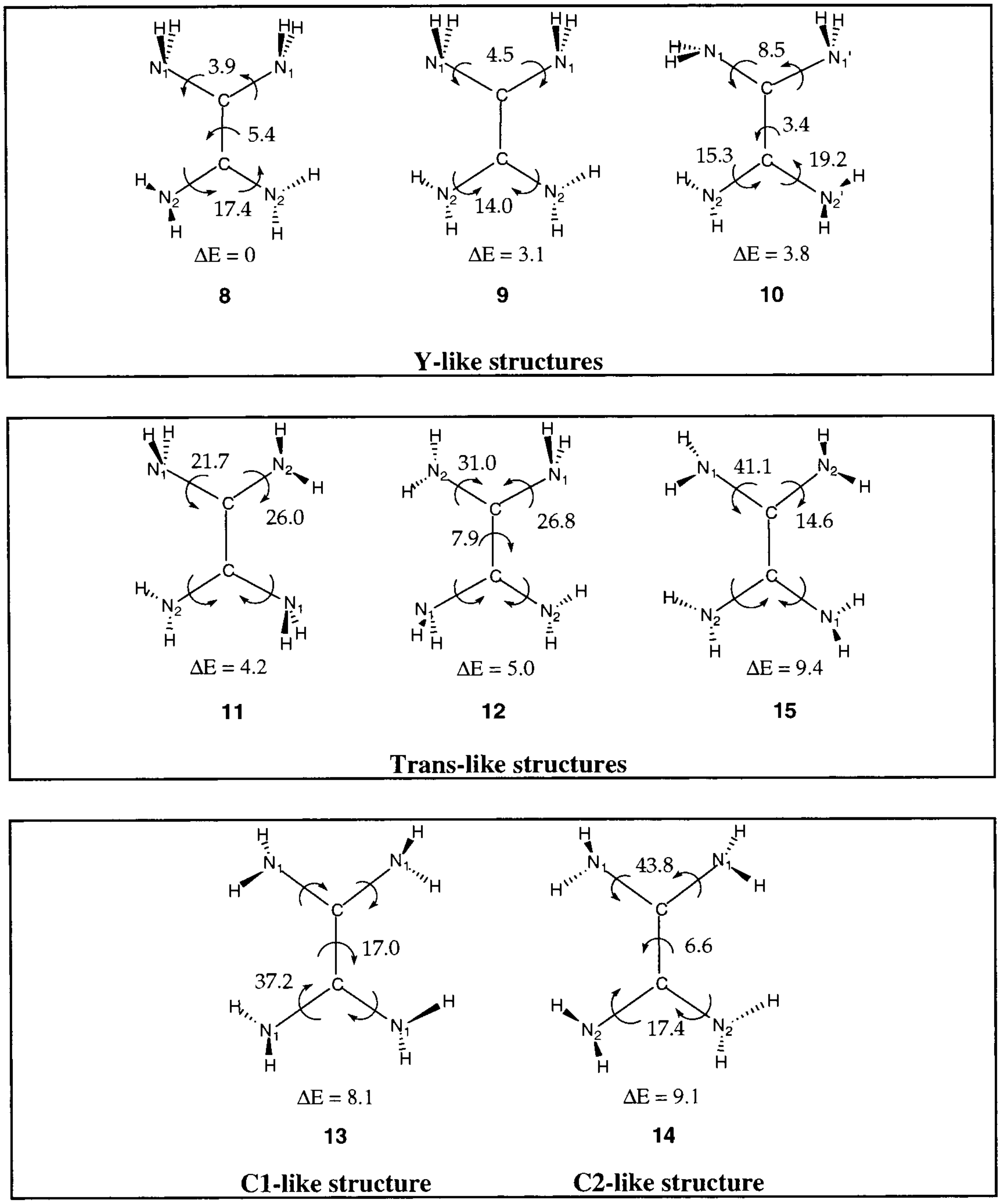


Figure 1. Optimized rotational angles (in deg) and relative energies (Δ*E*, in kcal/mol) of the minima **8**−**15** at the HF level. The *β* angle refers to the rotation of the top N_2C moiety with respect to the bottom one.

TABLE 6: Main Bond Lengths (in Å) and Relative Energies (ΔE_{MP2}, in kcal/mol) of the Five Idealized Structures 3−7 (MP2 level)

structure	C═C	CN_{conj}	CN_{deconj}	ΔE_{MP2}	ΔE_{HF}
3	1.348	1.410		0[a]	0
4	1.367		1.414	+5.5	+5.4
5	1.368	1.377	1.413	−20.6	−19.2
6	1.362	1.407	1.401	−10.9	−8.9
7	1.358	1.401	1.407	−16.0	−13.3

[a] Absolute energy: −298.992 04 au.

and 3.9 kcal/mol above **8**. The two minima **13** and **14** resulting from $\mathbf{C_1}$ and $\mathbf{C_2}$ motions are located 6.7 and 8.0 kcal/mol above the absolute minimum **8**, respectively. From a geometrical point of view, the different pair isomers exhibit almost the same bond lengths (Table 7). For instance, the CC distance varies from 1.354 to 1.357 Å within the three pair isomers of the Y-shaped

TABLE 7: Main Bond Lengths (in Å), Mean Pyramidalization Angles (*θ*, in deg), and Relative Energies (Δ*E*, in kcal/mol) of the Seven Optimized Structures 8−14 at the MP2 Level

	8	**9**	**10**	**11**	**12**	**13**	**14**
looks like	**5a**	**5b**	**5c**	**7a**	**7f**	**C1**	**C2**
Δ*E*	0[a]	3.5	3.5	3.1	3.9	6.7	8.0
C═C	1.355	1.357	1.354	1.351	1.352	1.354	1.352
CN_1[b]	1.437	1.437	1.433/1.435[c]	1.429	1.433	1.419	1.418
CN_2[b]	1.400	1.400	1.409/1.406[c]	1.419	1.419		1.424
θ_1[b]	126.8	126.9	126.3	125.0	123.5	131.5	135.2
θ_2[b]	127.2	129.8	128.6	124.6	125.6		123.5

[a] Absolute energy: −299.058 81 au, which corresponds to a stabilization of −41.9 kcal/mol with respect to **3**. [b] See Figure 2 for the definition of N_1, N_2 atoms. θ_1, θ_2 refer to pyramidalization angles of N_1 and N_2 atoms, respectively. [c] These two values correspond to the N_1 (N_2) and N_1' (N_2') atoms, see Figure 2.

TABLE 8: Main Bond Lengths (in Å) and Relative Energies (ΔE, in kcal/mol) of the Five Idealized Structures 3′−7′

structure	C═C	CN_{conj}	CN_{deconj}	ΔE
3′	1.455	1.483−1.567		211.9
4′	1.337		1.415	0[a]
5′	1.380	1.418	1.426	35.0
6′	1.365	1.426	1.419	19.5
7′	1.349	1.426	1.415	7.0

[a] Absolute energy: −610.303 13 au.

structure (**8**, **9**, and **10**). Only the orientation and the pyramidalization of the lone pairs noticeably differ from one isomer to another.

As found at the HF level, the MP2 results are clearly at odd with the experimental determination of the structure of the tetrakis(dimethylamino)ethylene. A geometry resembling the minimum **13** is experimentally found by both X-ray and electron diffraction (ED) methods, whereas we find a Y-shaped structure as absolute minimum. The energy difference (8.1 and 6.7 kcal/mol at HF and MP2 levels, respectively) is probably significant. The discrepancy between the experimental data and our theoretical results may originate from the replacement of the methyl groups by hydrogen atoms in our calculations. To check this point, calculations on the substituted tetrakis(dimethylamino)ethylene have been undertaken.

B. Substituted System $C_2(NMe_2)_4$. In the following, we will keep the notation used in unsubstituted systems study. A prime (′) will be added to characterize substitution by methyl groups. In a first step of calculation, idealized **3′**−**7′** geometries have been optimized at the HF level. The results are given in Table 8. Replacement of hydrogen atoms by methyl groups generates strong steric effects: the lowest energy structure is now the fully deconjugated one (**4′**) in which steric effects are expected to be the weakest. The fully conjugated one is less stable by more than 200 kcal/mol. Similarly, the Y-shaped structure **5′** is destabilized by 35 kcal/mol with respect to **4′**. Butadiene-like structures **6′** and **7′** in which steric effects are expected to be smaller are found to be at intermediate energies. From a geometrical point of view, the steric effects are clearly illustrated by the CC bond lengthening in **3′** (1.455 and 1.322 Å in methylated and unsubstituted species, respectively).

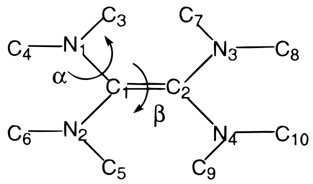
Starting from the geometries of the C_2N_4 moiety optimized in the unsubstituted species **8**−**15**, a full optimization has been undertaken for the substituted TDAE. Starting from the eight optimized structures at the HF level, only two minima, **8′**[13]

TABLE 9: Main Geometrical Parameters (Bond Lengths in Å, Angles in deg) of the Two Optimized Structures 8′ and 13′. See Scheme 5 for Atom Numbering

structural determination	X-ray 218 K	X-ray 90 K	ED	X-ray	theor. **8′**	theor. **13′**
reference	5	5	4	4	this work	this work
α	55[a]	48.7−51.1	55	55	19.8−48.6	51.0−59.2
β	28.3[a]	24.6	28	28.3	17.5	18.5
C_1-C_2	1.348	1.362	1.36[b]	1.351	1.342	1.340
C_1-N_1	1.410	1.415	1.403	1.399−1.408	1.406	1.416
C_1-N_2	1.399	1.410	1.403	1.399−1.408	1.406	1.413
C_2-N_3	1.397	1.414	1.403	1.399−1.408	1.424	1.413
C_2-N_4	1.412	1.411	1.403	1.399−1.408	1.424	1.416
N_1-C_3	1.434	1.448	1.452	1.411−1.451	1.441	1.446
N_1-C_4	1.443	1.455	1.452	1.411−1.451	1.446	1.444
N_2-C_5	1.415	1.444	1.452	1.411−1.451	1.441	1.444
N_2-C_6	1.441	1.442	1.452	1.411−1.451	1.446	1.442
N_3-C_7	1.420	1.444	1.452	1.411−1.451	1.444	1.444
N_3-C_8	1.438	1.451	1.452	1.411−1.451	1.448	1.442
N_4-C_9	1.413	1.447	1.452	1.411−1.451	1.448	1.446
N_4-C_{10}	1.453	1.454	1.452	1.411−1.451	1.444	1.444
$N_1-C_1-N_2$	112.6	114.9	118.4		110.7	115.0
$N_1-C_1-C_2$	124.7	125.0			124.6	120.0
$N_2-C_1-C_2$	122.7	120.1			124.6	124.8
Σ	360.0	359.9			360.0	359.8
$N_3-C_2-N_4$	114.2	115.3	118.4		120.7	115.0
$N_3-C_2-C_1$	121.8	120.2			119.6	124.8
$N_4-C_2-C_1$	124.0	124.5			119.6	120.0
Σ	360.0	360.0			360.0	359.8
$C_1-N_1-C_3$	119.4	119.2	119.2		121.3	118.8
$C_1-N_1-C_4$	118.6	116.3			117.3	117.5
$C_3-N_1-C_4$	115.2	113.5			114.0	113.9
Σ	353.2	349.0			352.6	350.2
$C_1-N_2-C_5$	122.1	119.5	119.2		121.3	117.6
$C_1-N_2-C_6$	120.1	119.3			117.3	120.4
$C_5-N_2-C_6$	117.7	115.5			114.0	113.9
Σ	359.9	354.4			352.6	351.9
$C_2-N_3-C_7$	121.3	118.8	119.2		117.6	117.6
$C_2-N_3-C_8$	120.5	118.1			117.6	120.4
$C_7-N_3-C_8$	117.3	114.3			113.4	113.9
Σ	359.1	351.2			348.6	351.9
$C_2-N_4-C_9$	121.0	119.6	119.2		117.6	118.8
$C_2-N_4-C_{10}$	117.9	116.3			117.6	117.5
$C_9-N_4-C_{10}$	116.2	113.9			113.4	113.9
Σ	355.1	349.8			348.6	350.2

[a] From ref 4. [b] Assumed.

SCHEME 5



and **13′**, have been located. All the other optimized minima collapse to only these two structures. No TS or *n*-SP have been found within this procedure. The lowest energy structure resembles the structure **8** found in the unsubstituted case. It can be viewed as a derivative of the idealized Y-shaped structure (**5′**) in which a rotation of the Me_2N groups has occurred ($\alpha(N_1) = \alpha(N_2) = 48.6°$, $\alpha(N_3) = \alpha(N_4) = -19.8°$, Table 9). The second minimum is located only 1.0 kcal/mol above the preceding minimum. It resembles the structure **13** found in the unsubstituted species and results from an almost synchronous conrotatory motion ($\alpha(N_1) = \alpha(N_4) = 59.2°$, $\alpha(N_2) = \alpha(N_3) = 51.0°$, Table 9).

Single-point calculations at the MP2 level have been performed on the HF-optimized geometries. The absolute minimum **8′**[14] found at the HF level remains the most stable structure, and **13′** becomes only 0.6 kcal/mol higher in energy at the MP2/HF level. Since both minima are close in energy, we have located the transition state of the interconversion. It lies 2.2 (HF level) and 3.5 kcal/mol (MP2/HF level) above the absolute minimum **8′**.

The main geometrical parameters of both optimized minima are reported in Table 9 together with the available experimental data. From the results in Table 9, it can be seen that the optimized structure **13′** is very close to that experimentally determined: for instance, the $C_{eth}-N$ bond lengths vary in the ranges 1.410−1.415 Å (exptl at 90 K) and 1.413−1.416 Å (theor.). The most important deviations are found for the C=C bond length (1.36 (exptl) vs 1.34 Å (theor.)) and the *β* twist

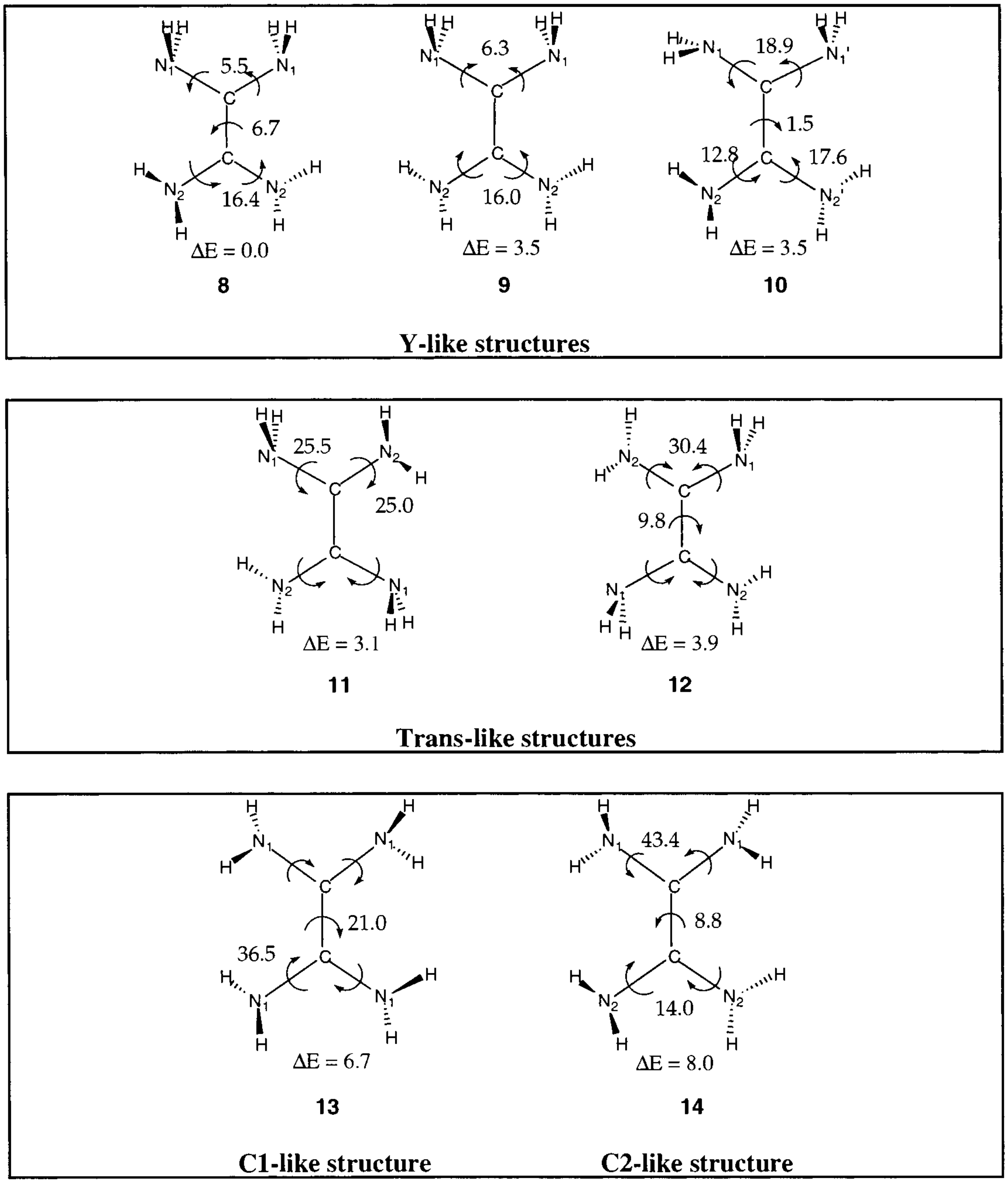


Figure 2. Optimized angles (in deg) and relative energies (Δ*E*, in kcal/mol) of the minima **8**−**14** at the MP2 level.

angle (24.6° (exptl) vs 18.5° (theor.)). These differences may be attributed in part to the calculation level: since geometry optimizations have been performed at the HF level, the CC bond length and the β twist angle are expected to be too small. Indeed, in the unsubstituted structure **13**, correlation effects lengthen the CC bond by about 0.03 Å (from 1.328 to 1.354 Å, Tables 5 and 7) and increase the β value from 17.0° to 21.0° (Figures 1 and 2).

However, the minimum **13′** is found to be located about 0.6 kcal/mol above the absolute minimum. This energy difference is hardly significant at our calculation level (MP2/HF), and the stability ordering cannot be firmly predicted from our results since this energy difference is too small. In addition, packing effects should be larger than the difference of stability between the two minima. It is thus reasonable that the experimentally observed geometry corresponds to our secondary minimum. In addition, it may be noted that the coexistence of two minima close in energy could well explain the phase transitions observed upon heating the crystal. Structural determination at lower temperatures (less than 90 K) should be of great interest.

Conclusion

Our study on TAE and TDAE shows that two factors (electronic and steric) are at work to understand the experimentally observed geometry in TDAE. In the unsubstituted molecule where the steric effects are the weakest, electronic effects dominate and a Y-shaped geometry is found to be the most stable. Other geometries deriving from the butadiene-like structures or from synchronous rotations of the amino groups are found to be higher in energy by 3−10 kcal/mol. When steric effects are taken into account in the eight-methylated system, they play an important role and only two minima are found. They are almost isoenergetical: the most stable structure can be viewed as deriving from an Y-shaped structure, whereas the second one resembles the minimum deriving from a conrotatory motion. The geometrical parameters of the latest are in excellent agreement with the experimental data. Finally, the coexistence of two isoenergetical minima for TDAE may explain the observed phase transitions in this material.

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(13) The absolute energy of **8′** is −610.340 29 au at the HF level. The stabilization of **8′** with respect to **4′** is equal to −23.3 kcal/mol.

(14) The absolute energy of **8′** is −612.314 08 au at the MP2/HF level.