

The Crystal and Molecular Structure of 2-Phenyl-4,5-dianilino-2*H*-1,2,3-triazole; Correlation between the Asymmetry of the Triazole Ring and the Conformations of the Anilino Substituents

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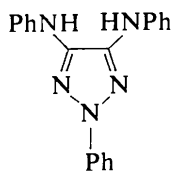
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2-Phenyl-4,5-dianilino-2*H*-1,2,3-triazole, $C_{20}H_{17}N_3$, crystallizes in the monoclinic system, space group $P2_1$, with $Z = 2$. At 23°C, $a = 5.782$ (1), $b = 9.582$ (1), $c = 16.114$ (1) Å, $\beta = 106.15$ (1)°, $D_x = 1.268$, $D_m = 1.276$ g cm⁻³. At -30°C, the temperature of the crystal during data collection, $a = 5.758$ (2), $b = 9.570$ (2), $c = 16.035$ (4) Å, $\beta = 105.85$ (3)°. Intensities were obtained from $\theta-2\theta$ scans with a Syntex $P2_1$ diffractometer using graphite-monochromated Mo $K\alpha$ radiation. The structure was solved by direct methods. Full-matrix least-squares refinement of all positional and thermal (anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms) parameters using 1398 reflections for which $I > 2\sigma(I)$ converged at a conventional R of 0.032. Although the molecule is symmetrically substituted with respect to the twofold axis, the triazole ring is found to be highly asymmetric. The chemically equivalent N–N bond distances, 1.312 (2) and 1.379 (2) Å, show the greatest disparity, although the C–N distances, 1.350 (2) and 1.320 (2) Å, are also significantly different. This distortion of the triazole ring is correlated *via* MINDO/3 calculations with the dissimilar conformations of the two anilino substituents, one of which is nearly coplanar with the triazole ring while the second is almost perpendicular to that ring.

Introduction

Although 1,2,4- and 1*H*-1,2,3-triazoles have been extensively studied by X-ray diffraction methods, there are apparently no reports of any structural investigations of 2*H*-1,2,3-triazoles. Thus, a structure determination of the title compound was undertaken because of crystallographic interest as well as for analytical identification. 2-Phenyl-4,5-dianilino-2*H*-1,2,3-triazole



was prepared by a thermal reaction of 1,1',3,3'-tetraphenylloxaldiamidrazone (structure reported by Harlow & Simonsen, 1975). It was expected that the pattern of substitution would maintain the twofold or mirror symmetry of the triazole ring with equivalent C–N and N–N bonds. However, the X-ray results revealed that the ring is highly distorted from 2 or m symmetry and suggested that this distortion was related to the different conformations found for the two anilino substituents.

Experimental

Colorless crystals of the triazole were grown by gradient sublimation. The crystal selected for this study had dimensions of 0.24 × 0.30 × 0.40 mm perpendicular to (0 $\bar{2}2$), (022), and ($\bar{1}12$) respectively. Mounted on a Syntex $P2_1$ diffractometer (Mo $K\alpha$ radiation, monochromated by a graphite crystal, $\lambda = 0.71069$ Å; equipped with a low-temperature apparatus which cooled the crystal to -30°C), the crystal was found to be monoclinic with systematic absences which were consistent with space groups $P2_1$ and $P2_1/m$. The unit-cell dimensions at -30°C were refined by the least-squares method using the Bragg angles of 29 reflections. The dimensions at 23°C were later determined

Table 1. Crystal data

	23°C	-30°C
2-Phenyl-4,5-dianilino-2 <i>H</i> -1,2,3-triazole		
$C_{20}H_{17}N_3$, FW 327.39, monoclinic, $P2_1$, $Z = 2$		
a (Å)	5.782 (1)	5.758 (2)
b (Å)	9.582 (1)	9.570 (2)
c (Å)	16.114 (1)	16.035 (4)
β (°)	106.15 (1)	105.85 (3)
V (Å ³)	857.6	850.1
D_x (g cm ⁻³)	1.268	
D_m (g cm ⁻³)	1.276	

from 23 reflections measured on a GE XRD-5 diffractometer with Cu $K\alpha_1$ radiation ($\lambda = 1.54050 \text{ \AA}$). Table 1 summarizes the crystal data.

Intensity data for 1600 unique reflections ($5^\circ < 2\theta < 50^\circ$) were collected with the Syntex diffractometer (crystal at -30°C) using the θ - 2θ scan technique. Each scan ranged from 1.0° in 2θ below the $K\alpha_1$ peak to 1.0° beyond the $K\alpha_2$ peak. The scan rate varied from 1.5 to $5.0^\circ \text{ min}^{-1}$ depending on the number of counts accumulated in a rapid preliminary scan of the peak. Background measurements were taken at both ends of the scan range, each for a time equal to half of the scan time. The intensities of four standard reflections were monitored after every 96 reflections; only statistical variations were noted. The intensities were corrected for Lorentz and polarization effects, but not for absorption ($\mu = 0.83 \text{ cm}^{-1}$).

Solution and refinement of the structure

The structure was solved by direct methods (*MULTAN*). Although the 'E' statistics were more indicative of a noncentrosymmetric space group, several futile attempts were made to solve the structure in the centrosymmetric space group $P2_1/m$; there are no steric restrictions which would prevent the molecule from exhibiting mirror symmetry. The structure was then solved in space group $P2_1$.

The full-matrix least-squares refinement of the structure using 1398 reflections for which $I > 2\sigma(I)$ converged smoothly to a conventional R of 0.032. Included in the 293 variables were all of the atomic coordinates, anisotropic thermal parameters for the non-hydrogen atoms, and isotropic thermal parameters for the hydrogen atoms. The largest shift in any variable during the final cycle of the refinement was 0.18σ . The final positional parameters are given in Table 2.* The largest peak in the final difference map had a magnitude of 0.11 e \AA^{-3} and was located in the center of the triazole ring. The mathematical and computational details are noted elsewhere (Harlow & Simonsen, 1976).

Discussion

The conformation and atom-numbering scheme for the molecule are shown in Fig. 1; each H atom is numbered in accord with the N or C atom to which it is bonded. Details of the molecular geometry are listed in Tables 3-5. The two outstanding features of this molecule are

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32700 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Atomic coordinates ($\times 10^4$, for H $\times 10^3$) for 2-phenyl-4,5-dianilino-2H-1,2,3-triazole

	x	y	z
N(1)	7324 (4)	4070 (4)	3185 (1)
N(2)	5687 (4)	3200*	3306 (1)
N(3)	3608 (4)	3112 (3)	2633 (1)
C(4)	4039 (5)	4007 (4)	2067 (2)
C(5)	6320 (5)	4614 (4)	2391 (2)
N(6)	2477 (5)	4325 (3)	1272 (2)
N(7)	7438 (5)	5609 (3)	1993 (2)
C(11)	6028 (5)	2390 (4)	4070 (2)
C(12)	8258 (5)	2384 (4)	4677 (2)
C(13)	8555 (6)	1572 (4)	5407 (2)
C(14)	6687 (6)	778 (4)	5529 (2)
C(15)	4503 (6)	810 (4)	4935 (2)
C(16)	4141 (5)	1621 (4)	4197 (2)
C(21)	293 (5)	3674 (4)	838 (2)
C(22)	-801 (6)	2649 (4)	1198 (2)
C(23)	-3018 (6)	2098 (5)	749 (2)
C(24)	-4163 (6)	2565 (5)	-65 (2)
C(25)	-3080 (6)	3592 (5)	-437 (2)
C(26)	-879 (7)	4141 (5)	4 (2)
C(31)	7751 (4)	6990 (3)	2290 (2)
C(32)	9465 (5)	7817 (4)	2075 (2)
C(33)	9744 (6)	9203 (4)	2331 (2)
C(34)	8316 (6)	9768 (5)	2803 (2)
C(35)	6606 (6)	8944 (4)	3017 (2)
C(36)	6302 (5)	7567 (4)	2763 (2)
H(6)	336 (5)	484 (3)	108 (2)
H(7)	856 (6)	526 (3)	184 (2)
H(12)	949 (5)	291 (3)	458 (2)
H(13)	1009 (6)	155 (4)	582 (2)
H(14)	705 (6)	18 (4)	604 (2)
H(15)	316 (6)	27 (4)	501 (2)
H(16)	268 (5)	163 (3)	381 (2)
H(22)	-13 (4)	231 (3)	172 (2)
H(23)	-381 (6)	131 (5)	103 (2)
H(24)	-574 (6)	224 (4)	-38 (2)
H(25)	-385 (6)	386 (4)	-101 (2)
H(26)	0 (7)	481 (4)	-16 (2)
H(32)	1047 (4)	741 (3)	177 (2)
H(33)	1101 (6)	977 (4)	220 (2)
H(34)	856 (5)	1073 (4)	299 (2)
H(35)	573 (5)	928 (4)	339 (2)
H(36)	516 (4)	700 (3)	290 (2)

* The space group requires the y coordinate of one atom to be fixed.

the significant asymmetry of the triazole ring and the dissimilar conformations of the anilino substituents. The discussion will thus be limited to these two characteristics and their apparent interrelationship.

The bond distances and angles listed in Table 3 agree, in general, with those previously reported. The values for the symmetrically substituted triazole ring are, however, unusual in that the chemically-equivalent C-N and N-N bonds differ by 0.030 and 0.067 \AA respectively (see Fig. 2a). The discrepancies in the N-C-C and N-N-C angles are not as striking but are still significant: 2.6 and 1.9° respectively.

It would seem reasonable that this distortion of the triazole ring is related to the only other unusual feature

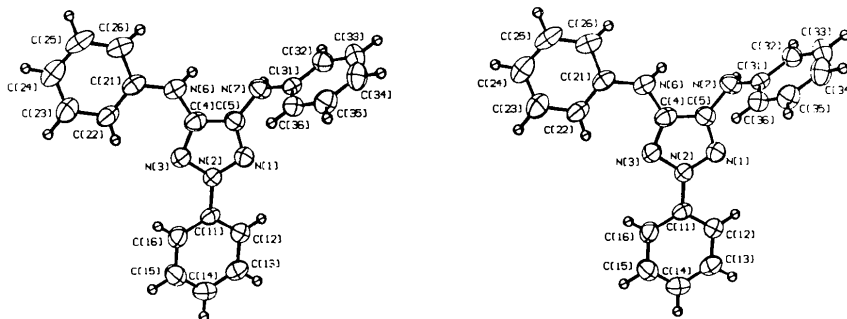


Fig. 1. Molecular geometry and atom-numbering scheme.

Table 3. Bond distances (Å) and angles (°) with estimated standard deviations

The C—H distances ranged from 0.89 to 1.04 Å with an average value of 0.95 Å. The C—C—H angles varied from 110 to 129° with an average value of 120°.

N(1)—N(2)	1.312 (2)	C(13)—C(14)	1.374 (5)
N(1)—C(5)	1.350 (4)	C(14)—C(15)	1.356 (5)
N(2)—N(3)	1.379 (2)	C(15)—C(16)	1.383 (5)
N(2)—C(11)	1.418 (3)	N(2)—C(22)	1.375 (5)
N(3)—C(4)	1.320 (4)	C(21)—C(26)	1.397 (4)
C(4)—C(5)	1.400 (4)	C(22)—C(23)	1.387 (5)
C(4)—N(6)	1.379 (4)	C(23)—C(24)	1.368 (5)
C(5)—N(7)	1.398 (4)	C(24)—C(25)	1.383 (6)
N(6)—C(21)	1.406 (4)	C(25)—C(26)	1.376 (5)
N(6)—H(6)	0.82 (3)	C(31)—C(32)	1.381 (4)
N(7)—C(31)	1.400 (4)	C(31)—C(36)	1.388 (4)
N(7)—H(7)	0.82 (3)	C(32)—C(33)	1.385 (5)
C(11)—C(12)	1.384 (4)	C(33)—C(34)	1.373 (5)
C(11)—C(16)	1.373 (4)	C(34)—C(35)	1.377 (5)
C(12)—C(13)	1.377 (4)	C(35)—C(36)	1.377 (6)
N(2)—N(1)—C(5)	104.2 (2)	C(12)—C(13)—C(14)	120.9 (2)
N(1)—N(2)—N(3)	115.4 (1)	C(13)—C(14)—C(15)	120.0 (3)
N(1)—N(2)—C(11)	122.7 (1)	C(14)—C(15)—C(16)	120.6 (3)
N(3)—N(2)—C(11)	121.9 (1)	C(11)—C(16)—C(15)	119.2 (3)
N(2)—N(3)—C(4)	102.3 (2)	N(6)—C(21)—C(22)	124.0 (3)
N(3)—C(4)—C(5)	110.4 (2)	N(6)—C(21)—C(26)	117.7 (3)
N(3)—C(4)—N(6)	125.5 (3)	C(22)—C(21)—C(26)	118.3 (3)
C(5)—C(4)—N(6)	124.1 (3)	C(21)—C(22)—C(23)	121.0 (3)
N(1)—C(5)—C(4)	107.8 (3)	C(22)—C(23)—C(24)	120.5 (3)
N(1)—C(5)—N(7)	124.2 (3)	C(23)—C(24)—C(25)	119.2 (3)
C(4)—C(5)—N(7)	128.0 (3)	C(24)—C(25)—C(26)	120.7 (3)
C(4)—N(6)—C(21)	129.0 (3)	C(21)—C(26)—C(25)	120.4 (3)
C(4)—N(6)—H(6)	99 (2)	N(7)—C(31)—C(32)	119.4 (2)
C(21)—N(6)—H(6)	130 (2)	N(7)—C(31)—C(36)	121.4 (3)
C(5)—N(7)—C(31)	121.4 (2)	C(32)—C(31)—C(36)	119.1 (3)
C(5)—N(7)—H(7)	111 (2)	C(31)—C(32)—C(33)	120.5 (3)
C(31)—N(7)—H(7)	117 (2)	C(32)—C(33)—C(34)	120.2 (3)
N(2)—C(11)—C(12)	119.6 (2)	C(33)—C(34)—C(35)	119.3 (4)
N(2)—C(11)—C(16)	119.6 (2)	C(34)—C(35)—C(36)	121.1 (3)
C(12)—C(11)—C(16)	120.9 (3)	C(31)—C(36)—C(35)	119.7 (3)
C(11)—C(12)—C(13)	118.5 (3)		

of the molecule, namely the contrasting orientations of the two anilino substituents. The first anilino group, composed of atoms N(6) and C(21) to C(26), is nearly coplanar with the triazole ring (Fig. 1, Tables 4 and 5). The second group, composed of N(7) and C(31) to

C(36), is almost perpendicular to the triazole ring. Although both N atoms are π conjugated with their respective phenyl groups, only N(6) can π conjugate with the triazole ring. The differences in the bond lengths associated with N(6) and its chemical equivalent, N(7), reflect this dissimilarity in bonding. In addition, the coplanarity of the first anilino group and the triazole ring produces a close intramolecular contact between H(22) and N(3); the resulting repulsion is relieved by increasing the N(3)—C(4)—N(6), C(4)—N(6)—C(21), and N(6)—C(21)—C(22) angles (compare chemically-equivalent angles in Fig. 2a).

In an effort to correlate the conformations of the anilino groups with the distortion of the triazole ring, molecular-orbital calculations, MINDO/3 (Bingham, Dewar & Lo, 1975), were carried out on a model compound in which the phenyl substituent was replaced with a H atom. In the first instance, the geometry of the molecule was optimized with no restrictions, *i.e.* all bond distances, angles, and torsion angles were treated as variables. This calculation produced a molecule with virtual twofold symmetry; the two anilino groups had rotated by about 40° in opposite directions out of the triazole plane. All chemically-equivalent bond distances and angles were found to be equal. In the second calculation, the torsion angles relating the coplanar anilino group to the triazole ring were fixed at the values determined by the X-ray structure. The torsion angles for the second anilino group were also initialized at the X-ray values, and, although these were allowed to vary, this group remained approximately perpendicular to the triazole ring. The resulting bond distances and angles for this conformation are given in Fig. 2(b). MINDO/3 normally reproduces bond lengths with a mean error of ± 0.02 Å, but, for reasons associated with the INDO approximation, larger errors occur in the case of compounds containing N—N bonds. While the differences between the calculated and observed bond lengths in the present compound are consequently somewhat larger than usual, it is interesting and significant that MINDO/3 does reproduce the trend of distortions in the five-membered ring observed in the X-ray structure.

Table 4. Selected torsion angles ($^{\circ}$)

The right- and left-hand columns are arranged to contrast the two chemically-equivalent halves of the molecule. If the molecule possessed mirror symmetry, each pair of angles would have equal magnitudes but opposite signs.

(a) The triazole ring

C(5)–N(1)–N(2)–N(3)	0.4	C(4)–N(3)–N(2)–N(1)	–0.4
N(2)–N(1)–C(5)–C(4)	–0.2	N(2)–N(3)–C(4)–C(5)	0.2
N(3)–C(4)–C(5)–N(1)	0.0		

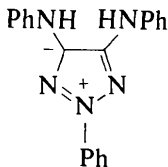
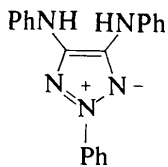
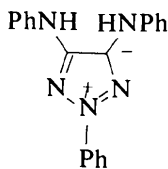
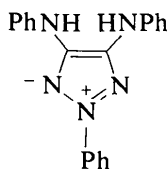
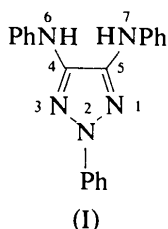
(b) Triazole ring to phenyl substituent

C(5)–N(1)–N(2)–C(11)	179.6	C(4)–N(3)–N(2)–C(11)	–179.6
N(1)–N(2)–C(11)–C(12)	–7.4	N(3)–N(2)–C(11)–C(16)	–8.2
N(1)–N(2)–C(11)–C(16)	172.6	N(3)–N(2)–C(11)–C(12)	171.8

(c) Triazole ring to anilino substituents

N(2)–N(1)–C(5)–N(7)	179.7	N(2)–N(3)–C(4)–N(6)	–179.1
N(1)–C(5)–C(4)–N(6)	179.3	N(3)–C(4)–C(5)–N(7)	–179.9
N(6)–C(4)–C(5)–N(7)	–0.6		
N(1)–C(5)–N(7)–C(31)	–70.9	N(3)–C(4)–N(6)–C(21)	–9.1
N(1)–C(5)–N(7)–H(7)	72	N(3)–C(4)–N(6)–H(6)	–173
C(4)–C(5)–N(7)–C(31)	109.0	C(5)–C(4)–N(6)–C(21)	171.6
C(4)–C(5)–N(7)–H(7)	–108	C(5)–C(4)–N(6)–H(6)	6
C(5)–N(7)–C(31)–C(32)	160.0	C(4)–N(6)–C(21)–C(22)	7.1
C(5)–N(7)–C(31)–C(36)	–22.9	C(4)–N(6)–C(21)–C(26)	–175.7
H(7)–N(7)–C(31)–C(32)	19	H(6)–N(6)–C(21)–C(22)	169
H(7)–N(7)–C(31)–C(36)	–164	H(6)–N(6)–C(21)–C(26)	–14

The asymmetric geometry of the triazole ring can be pictured from some of the possible resonance structures:



In order to be consistent with the X-ray results, which show that the N(1)–N(2) and N(3)–C(4) distances are shorter than their chemical counterparts, N(2)–N(3)

Table 5. Deviations (\AA) from various least-squares mean planes

(I) Plane of the triazole ring: N(1), N(2), N(3), C(4), C(5)

N(1)	0.002 (2)	C(5)	–0.001 (3)	C(11)	0.007 (3)
N(2)	–0.002 (3)	N(6)	–0.016 (3)	C(21)	0.141 (3)
N(3)	0.001 (3)	N(7)	–0.004 (3)	C(22)	0.207 (4)
C(4)	–0.001 (3)				

(II) Plane of the phenyl substituent: C(11) to C(16)

C(11)	0.008 (3)	C(14)	0.008 (4)	C(16)	–0.006 (4)
C(12)	–0.002 (4)	C(15)	–0.002 (4)	N(2)	0.034 (1)
C(13)	–0.006 (4)				

(III) Plane of the phenyl group associated with the first anilino substituent: C(21) to C(26)

C(21)	–0.003 (3)	C(24)	–0.001 (4)	N(6)	–0.069 (3)
C(22)	0.001 (4)	C(25)	–0.001 (4)	H(6)	0.05 (3)
C(23)	0.001 (4)	C(26)	0.003 (3)	C(4)	–0.007 (3)

(IV) Plane of the phenyl group associated with the second anilino substituent: C(31) to C(36)

C(31)	–0.003 (2)	C(34)	–0.001 (4)	N(7)	0.050 (3)
C(32)	0.000 (3)	C(35)	–0.003 (3)	H(7)	–0.16 (3)
C(33)	0.002 (3)	C(36)	0.005 (3)	C(5)	–0.356 (3)

Dihedral angles: (I)–(II) = 7.9° ; (I)–(III) = 3.8° ; (I)–(IV) = 84.5°

and N(1)–C(5), one can propose that resonance forms II and III make larger contributions to the structure than do IV and V. This proposal is substantiated by the second MINDO/3 calculation which indicates higher electron populations for N(3) and C(5) than for N(1) and C(4).

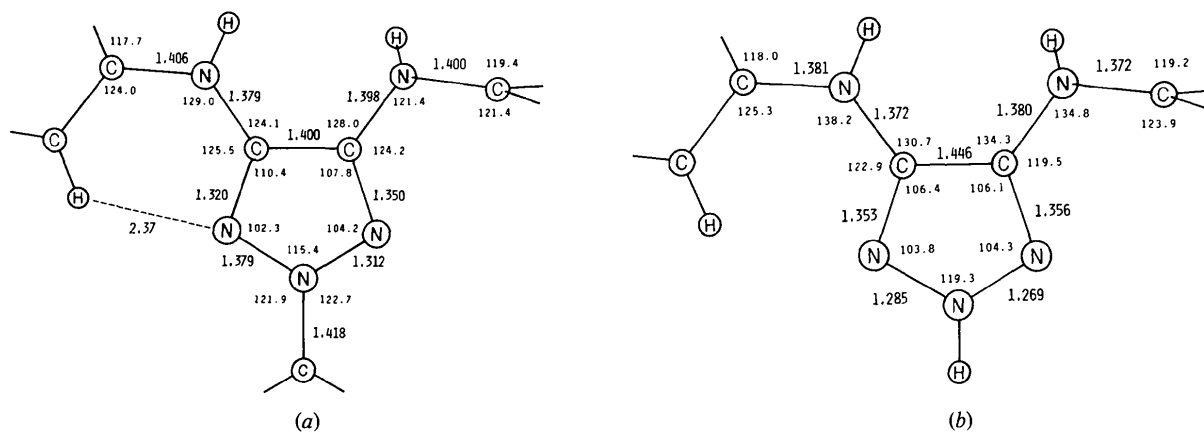


Fig. 2. A comparison of the bond parameters for the triazole ring system: (a) the X-ray results, (b) the results of the MINDO/3 calculation in which one of the anilino groups was fixed to be nearly coplanar with the triazole ring.

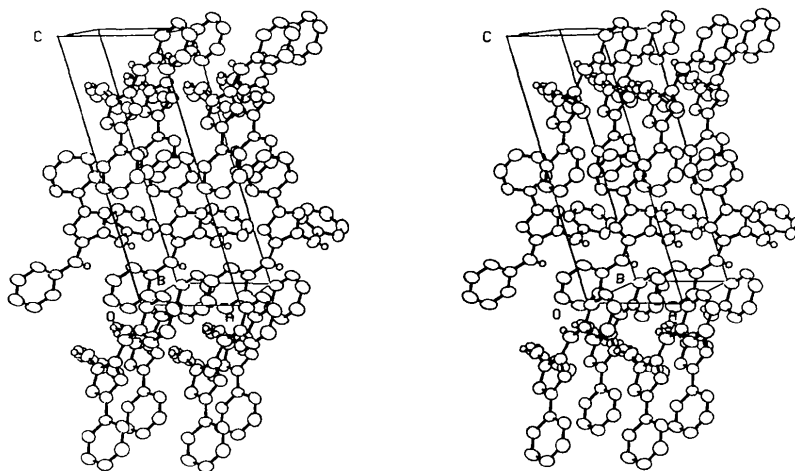


Fig. 3. Packing diagram for 2-phenyl-4,5-dianilino-2H-1,2,3-triazole. The H atoms bonded to the three phenyl groups have not been included.

Although the energy difference for the two conformations is computed to be <1 kcal, the symmetric conformation is found to be more stable. This suggests that the asymmetric geometry found in the crystalline state exists as a result of 'packing forces'. An examination of the intermolecular distances reveals that the shortest contacts occur between molecules related by a translation parallel to the a axis (see Fig. 3): C(4) \cdots C(23)', 3.555 (4); C(5) \cdots C(22)', 3.418 (4); N(7) \cdots C(21)', 3.351 (4); N(7) \cdots C(22)', 3.374 (5) Å. These interactions between the anilino group of one molecule and the triazole ring of a neighboring molecule might be interpreted as part of the packing forces necessary to keep the anilino group coplanar with the triazole ring. Despite the potential for N-H \cdots N intermolecular hydrogen bonding, such bonding does not exist in the crystal structure and

hence cannot play a role in determining the conformations of the anilino groups. The shortest H \cdots N contact, 2.80 (3) Å between H(7) and N(6)[1 + x , y , z], is much too long for a significant interaction.

The small difference in calculated energies for the symmetric and asymmetric conformations suggests that X-ray structures of suitable derivatives of the present molecule may show that both conformations are possible in the crystalline state. 2H-1,2,3-Triazoles with symmetrically and asymmetrically substituted anilino groups are presently being synthesized for further investigations. Conformational studies of the molecule in the gaseous state and in solution are also under consideration.

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Structures de Six Sels de Dérivés du Cyclobuténylidèneammonium

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The structures of six cyclobutenylideneammonium salts, (CBA)⁺X⁻, were solved by direct methods and refined by block-diagonal least squares, from diffractometer intensities. *N,N*-Dimethyl-3-dimethylamino-2,4-diethyl(CBA) perchlorate (I) is monoclinic, $P2_1/c$ with $a = 7.910$ (2), $b = 20.677$ (5), $c = 11.889$ (3) Å, $\beta = 128.12$ (2)°, $Z = 4$. *N,N*-Dimethyl-3-dimethylamino-2,4-di(*tert*-butyl)(CBA) chloride (II) is orthorhombic, $Pnma$ with $a = 11.070$ (3), $b = 10.091$ (3), $c = 15.163$ (4) Å, $Z = 4$. *N,N*-Diethyl-3-diethylamino-2,4-diphenyl(CBA) perchlorate (III) is monoclinic, $P2_1/c$ with $a = 19.038$ (5), $b = 7.946$ (2), $c = 17.595$ (4) Å, $\beta = 113.67$ (2)°, $Z = 4$. *N,N*-Diethyl-3-diethylamino-4-methyl-2,4-bis(phenylthio)(CBA) perchlorate (IV) is monoclinic, $P2_1/n$ with $a = 28.545$ (6), $b = 9.491$ (3), $c = 10.013$ (3) Å, $\beta = 97.26$ (2)°, $Z = 4$. *N,N*-Dimethyl-2-(*tert*-butyl)-4,4-dimethyl(CBA) tetrafluoroborate (V) is orthorhombic, $Pna2_1$ with $a = 17.591$ (4), $b = 9.536$ (3), $c = 8.787$ (3) Å, $Z = 4$. *N,N*-Dimethyl-2,3,4,4-tetramethyl(CBA) perchlorate (VI) is orthorhombic, $P2_12_12_1$ with $a = 14.306$ (4), $b = 10.867$ (3), $c = 8.387$ (3) Å, $Z = 4$. Except for (I), all H atoms, located on difference syntheses, were refined isotropically. (V) and (VI) are true CBA derivatives but the first four compounds are symmetrical cyclobutenecyanines, owing to the presence of a dialkylamino group on position 3.

Introduction

Le présent travail rassemble et compare les observations structurales que nous avons faites sur les six dérivés nouveaux du cyclobutène énumérés dans le Tableau 1. Les quatre premiers sont les sels de cyclobutenecyanines synthétisées par Notté (1976) et Houtekie (1977) au Laboratoire de Chimie Organique de Synthèse de l'Université de Louvain (Professeur L. Ghosez). Les deux derniers sont des sels de cyclobuténylidèneammonium (ou cyclobuténeiminium) provenant du même laboratoire (Hoornaert, Hesbain-Frisque & Ghosez, 1975).

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Données expérimentales, résolution et affinement des structures

Le Tableau 2 résume les principales données physiques et cristallographiques. Les paramètres réticulaires ont été mesurés sur les diffractomètres mentionnés au Tableau 3. Ce même tableau indique également les conditions d'enregistrement des spectres de diffraction ainsi que les caractéristiques des processus de résolution et d'affinement des structures. Toutes les résolutions ont été obtenues par la méthode de multi-solution à l'aide du système de programmes *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974). Les affinements ont été menés dans l'approximation des blocs diagonaux selon les programmes *NRC-10* de Ahmed, Hall, Pippy & Huber (1966) avec des schémas de pondération faisant intervenir des poids