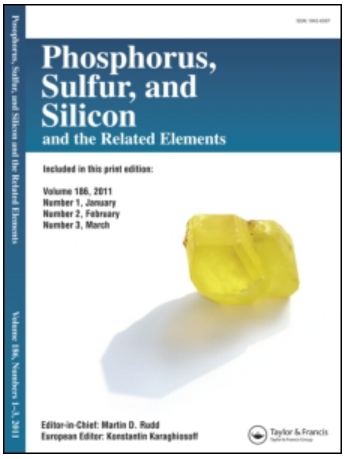

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X-RAY CRYSTAL STRUCTURE, DIPOLE MOMENT AND THEORETICAL MOLECULAR ORBITAL STUDY OF 5-NITRO-2- (2-PYRIDINYLTHIO)-PYRIDINE

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X-RAY CRYSTAL STRUCTURE, DIPOLE MOMENT AND THEORETICAL MOLECULAR ORBITAL STUDY OF 5-NITRO-2-(2-PYRIDINYLTHIO)-PYRIDINE

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The conformational aspects of 5-nitro-2-(2-pyridinylthio)-pyridine were investigated in the three states of matter. The experimentally derived conformers using the analytical methods (X-ray diffraction, dipolometry) are compared with theoretical MO calculations (AM-1 method). Crystals are monoclinic, with unit cell dimensions $a = 6.081(5)$, $b = 15.131(8)$, $c = 22.549(10)$ Å; $\beta = 93.40(5)°$; space group $P2_1/c$. The structure was determined from 2243 three dimensional counter data and refined to convergence factor values of $R = 0.08$. Two independent molecules (*A* and *B*) there are per asymmetric unit, which are similar as concern the bond lengths and angles close to usual standard values. In both *A* and *B* the 5-nitro-pyridine ring (bearing nitrogen atom N(2)) is rotated out by 12° of coplanarity with C–S–C plane, while the pyridine ring (bearing nitrogen atom N(1)) is twisted, in a disrotatory way, by 41.7° (*A*) and 59.7° (*B*). The relative orientations of the ring nitrogen atoms with respect to the C–S–C angle, are N(1), N(2)-*outside* and N(1)-*inside*/N(2)-*outside*, in *A* and *B*, respectively. The dipole moment analysis indicates that the twisted conformation of the solid *A* should be retained in solution. The twisted conformations in the solid and in solution do not parallel the minimum energy conformation calculated for the isolated molecule by AM-1 method, in which the two rings are rotated in opposite directions out of the all-planar N(1), N(2)-*inside* conformation by 36° (5-nitro-pyridine ring) and 54° (pyridine ring).

Key words: 5-Nitro-2-(2-pyridinylthio)-pyridine; X-Ray-diffraction; dipole moment; MO-calculations.

INTRODUCTION

The conformational properties and the molecular structure of sulphur-bridged hetero-aromatic molecules, such as di-2-pyridinylsulphide (generic name for 2-(2-pyridinylthio)-pyridine) and its substituted analogues, are of importance in view of their applications in medicinal chemistry[1] and in polymer chemistry.[2] The above compound, which has low melting point, was previously investigated by using both physical and theoretical methods in solution and in gas phases.[3–8] The crystals suited for the determination of molecular structure and conformation in the solid were only attainable from its 5-nitro derivative compound, 5-nitro-2-(2-pyridinylthio)-pyridine (NPTP).

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Both experimental (X-ray diffraction study of the crystal and dipole moment measurement and analysis) and theoretical methods (MO semiquantitative calculations AM-1 type) were therefore applied here to elucidate the conformation of NPTP and to obtain quantitative comparison of the gaseous, fluid and solid state conformation of this molecule. From the methodological point of view combined methods are of great utility for the study of conformational problems and, in particular, for investigating the influence of the factors which determine the molecular conformation in the three aggregation states.

EXPERIMENTAL

Sample. NPTP was synthesized using the lit. method[9] and crystallized from aqueous ethanol (m.p. 103–4°C).

Crystal Structure Determination. A crystal with dimensions *ca.* 0.15 × 0.25 × 0.35 mm was mounted on a glass capillary and transferred to a Philips PW 1100 computer-controlled diffractometer.

TABLE I

Fractional atomic coordinates with e.s.d.'s in parentheses

Molecule *A*			
Atom	*x*	*y*	*z*
S(1)	0.3171(3)	0.6969(2)	0.1179(1)
O(1)	0.9258(9)	0.5394(5)	−0.0917(3)
O(2)	0.6035(10)	0.5512(5)	−0.1368(3)
N(1)	0.4671(13)	0.7136(6)	0.2280(3)
N(2)	0.3294(9)	0.6410(4)	0.0113(3)
N(3)	0.7268(10)	0.5578(4)	−0.0932(3)
C(1)	0.6023(20)	0.7434(8)	0.2722(4)
C(2)	0.7920(17)	0.7916(6)	0.2635(4)
C(3)	0.8319(16)	0.8082(7)	0.2048(5)
C(4)	0.6999(14)	0.7805(6)	0.1595(4)
C(5)	0.5145(13)	0.7331(5)	0.1726(3)
C(6)	0.4636(11)	0.6538(5)	0.0588(3)
C(7)	0.6935(11)	0.6350(5)	0.0626(3)
C(8)	0.7788(11)	0.6028(5)	0.0188(3)
C(9)	0.6441(11)	0.5916(5)	−0.0375(3)
C(10)	0.4156(11)	0.6078(5)	−0.0375(3)
Molecule *B*			
Atom	*x*	*y*	*z*
S(2)	0.4301(3)	0.5078(2)	−0.3819(1)
O(3)	0.1362(10)	0.7467(4)	−0.6114(3)
O(4)	−0.1940(10)	0.7310(4)	−0.5807(3)
N(4)	0.0615(10)	0.4425(5)	−0.3390(3)
N(5)	0.4091(9)	0.6010(4)	−0.4772(3)
N(6)	0.0043(12)	0.7161(5)	−0.5769(3)
C(11)	−0.0713(13)	0.4250(6)	−0.2943(4)
C(12)	−0.0183(14)	0.4508(6)	−0.2368(4)
C(13)	0.1687(16)	0.4961(7)	−0.2236(4)
C(14)	0.3113(13)	0.5167(6)	−0.2683(4)
C(15)	0.2443(11)	0.4882(5)	−0.3245(3)
C(16)	0.2768(10)	0.5670(5)	−0.4373(3)
C(17)	0.0486(11)	0.5787(5)	−0.4410(3)
C(18)	−0.0427(10)	0.6267(5)	−0.4872(3)
C(19)	0.0950(12)	0.6632(5)	−0.5278(3)
C(20)	0.3170(12)	0.6461(5)	−0.5222(3)

The crystal data were: $C_{10}H_7N_3O_2S$, $M = 233.2$, monoclinic, $a = 6.081(5)$, $b = 15.131(8)$, $c = 22.549(10)$ Å, $\beta = 93.40(5)°$, $U = 2071.1(2.0)$ Å^3, $Z = 8$, $D_c = 1.496$ gcm^{-3}, $F(000) = 960$, μ (MoKα radiation, $\lambda = 0.7170$ Å) $= 2.8$ cm^{-1}, space group $P2_1/c$.

A unique data set was collected at 20°C by using a $\omega - 2\vartheta$ scan mode for all reflections for which $3 < 2\vartheta < 50°$, a scan range of 1.2°, a scan rate of 0.04° s^{-1} and a total background time of 14 s. Three standard reflections were measured every 2h, the intensities of which did not exhibit any systematic trend throughout the data collection. The intensities of 3744 independent reflections were measured but only 2243 obeyed the condition $I > 3\sigma(I)$ and were used in subsequent calculations. The data were corrected for Lorentz and polarization effects, but not for extinction or absorption. The structure was solved by direct methods and the set with the highest consistency index was used to produce an E map, from which the asymmetric unit appears to contain two independent molecules (A and B). A number of cycles of least-squares refinement, with anisotropic thermal parameters in the last stage, followed by difference syntheses, enabled location for all non-hydrogen atoms and led to convergence with $R = 0.08$. A difference map at this point did not yield all 14 hydrogen atoms, their fractional coordinates were generated from geometry but were not included in the structure factor calculations. The function $\sum w(|F_0| - |F_c|)^2$ was minimized, with unit weights. Final positional parameters are listed in Table I; bond distances and angles are given in Table II, while some other geometrical data are

TABLE II

Bond distances (Å) and bond angles (°) for NPTP (e.s.d.'s average 0.02 Å and 1.5°, respectively)

Molecule *A*		Molecule *B*	
S(1)–C(5)	1.76	S(2)–C(15)	1.79
S(1)–C(6)	1.77	S(2)–C(16)	1.76
N(1)–C(1)	1.33	N(4)–C(11)	1.35
C(1)–C(2)	1.39	C(11)–C(12)	1.37
C(2)–C(3)	1.38	C(12)–C(13)	1.35
C(3)–C(4)	1.33	C(13)–C(14)	1.40
C(4)–C(5)	1.38	C(14)–C(15)	1.38
N(1)–C(5)	1.33	N(4)–C(15)	1.33
C(6)–C(7)	1.42	C(16)–C(17)	1.40
C(7)–C(8)	1.37	C(17)–C(18)	1.36
C(8)–C(9)	1.35	C(18)–C(19)	1.39
C(9)–C(10)	1.41	C(19)–C(20)	1.32
C(10)–N(2)	1.34	C(20)–N(5)	1.32
N(2)–C(6)	1.32	N(5)–C(16)	1.34
C(9)–N(3)	1.47	C(19)–N(6)	1.45
N(3)–O(1)	1.24	N(6)–O(3)	1.24
N(3)–O(2)	1.20	N(6)–O(4)	1.22
C(5)–S(1)–C(6)	106.9	C(15)–S(2)–C(16)	105.4
S(1)–C(5)–N(1)	114.4	S(2)–C(15)–N(4)	117.5
S(1)–C(5)–C(4)	122.9	S(2)–C(15)–C(14)	116.6
N(1)–C(5)–C(4)	122.7	N(4)–C(15)–C(14)	125.7
C(5)–N(1)–C(1)	118.0	C(15)–N(4)–C(11)	116.4
N(1)–C(1)–C(2)	123.5	N(4)–C(11)–C(12)	122.0
C(1)–C(2)–C(3)	155.2	C(11)–C(12)–C(13)	120.1
C(2)–C(3)–C(4)	123.1	C(12)–C(13)–C(14)	120.2
C(3)–C(4)–C(5)	117.6	C(13)–C(14)–C(15)	115.5
S(1)–C(6)–N(2)	110.5	S(2)–C(16)–N(5)	110.9
S(1)–C(6)–C(7)	124.4	S(2)–C(16)–C(17)	126.2
N(2)–C(6)–C(7)	125.1	N(5)–C(16)–C(17)	122.9
C(6)–C(7)–C(8)	116.0	C(16)–C(17)–C(18)	118.2
C(7)–C(8)–C(9)	119.3	C(17)–C(18)–C(19)	118.8
C(8)–C(9)–C(10)	121.8	C(18)–C(19)–C(20)	119.5
C(9)–C(10)–N(2)	119.7	C(19)–C(20)–N(5)	122.5
C(10)–N(2)–C(6)	117.8	C(20)–N(5)–C(16)	118.0
C(8)–C(9)–N(3)	121.6	C(18)–C(19)–N(6)	120.3
C(10)–C(9)–N(3)	116.5	C(20)–C(19)–N(6)	120.1
C(9)–N(3)–O(1)	115.9	C(19)–N(6)–O(3)	117.1
C(9)–N(3)–O(2)	119.8	C(19)–N(6)–O(4)	118.9
O(1)–N(3)–O(2)	124.3	O(3)–N(6)–O(4)	123.9

TABLE III

Some relevant geometrical entities

	Molecule *A*		Molecule *B*	
(a)	Torsion angles (°)			
	C(5)–S(1)–C(6)–N(2) (ω_1) −167.9		C(15)–S(2)–C(16)–N(5) (ω_1) 167.5	
	N(1)–C(5)–S(1)–C(6) (ω_2) −138.3		N(4)–C(15)–S(2)–C(16) (ω_2) 59.7	
(b)	Least-squares planes and deviation (Å) of relevant atoms in squares brackets			
	(1) N(1), C(1), C(2), C(3), C(4), C(5)		(4) N(4), C(11), C(12), C(13), C(14), C(15)	
	S(1) −0.09; C(6) 1.02		S(2) −0.09; C(16) 1.31	
	(2) N(2), C(6), C(7), C(8), C(9), C(10)		(5) N(5), C(16), C(17), C(18), C(19), C(20)	
	S(1) 0.03; C(5) 0.39		S(2) −0.01; C(15) −0.38	
	(3) C(9), N(3), O(1), O(2)		(6) C(19), N(6), O(3), O(4)	
(c)	Angles between the planes (°)			
	(1)–(2)	132.7	(4)–(5)	125.6
	(1)–(3)	131.4	(4)–(6)	120.1
	(2)–(3)	2.8	(5)–(6)	1.7
(d)	Some interatomic contacts (Å)			
	C(8) · · · O(1)	2.72	C(18) · · · O(4)	2.75
	C(10) · · · O(2)	2.71	C(20) · · · O(3)	2.70
	C(4) · · · C(7)	3.10	N(4) · · · C(17)	3.09
	N(1) · · · N(2)	5.03	N(4) · · · N(5)	4.55

reported in Table III. The atom numbering scheme and molecular packing are shown in Figures 1 and 2, respectively. Lists of structure factors and thermal parameters have been deposited as Supplementary Material. The major calculations were made with the SHELXS-86 program-package.[10]

Dipole Moment. The electric dipole moment μ of NPTP was measured at 25 ± 0.01°C in benzene solution as described earlier.[11] The experimental value ($\mu_{exp} = 4.84$ D) was calculated from the total solute polarization ($P_{2\infty} = 540.3\,cm^3$) obtained by extrapolation to infinite dilution according to the Halverstadt–Kumler method[12] and from the molar refraction ($R_D = 60.3\,cm^3$) which was considered to be equal to the electronic and atomic polarization ($P_e + P_a$). The other polarization data were: $\alpha = 11.09$; $\beta = -0.390$. The estimated accuracy of μ_{exp} value was ±0.02 D.

Theoretical Calculations. Quantum chemical AM-1 type[13] calculations of conformational energies were performed using the AMPAC package[14] run on a Digital VAX 11/750 computer system. The geometric parameters used came from the X-ray crystal structure data. The rotational angles ω_1, ω_2 were independently varied, with a scanning of 18°, by initially assuming the molecule to be a rigid rotor and the all-planar N-inside conformation as the one for which $\omega_1 = \omega_2 = 0°$ (Figure 3). Full optimization both of geometry and ω_1, ω_2 values was carried out by the AM-1 method within each

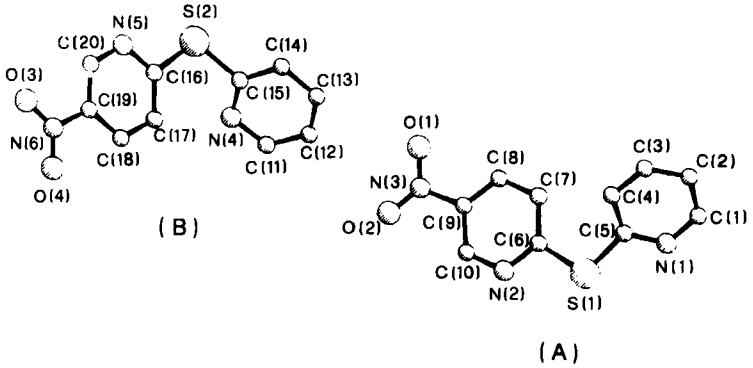

FIGURE 1 A projection of the asymmetric unit, containing *A* and *B* molecules, down the *b*-axis. The atom numbering scheme is also shown.

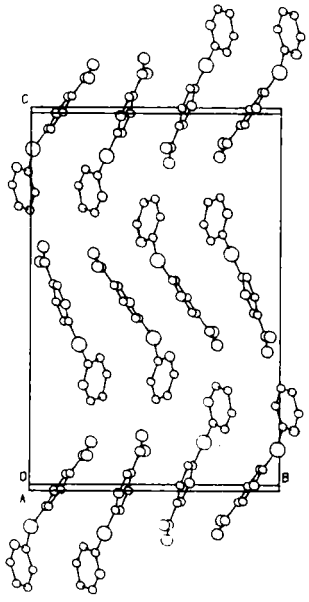

FIGURE 2 Packing of the molecules in the unit cell. The *b* and *c* axes are parallel to the bottom and side of the page, respectively, and the view is along the *a*-axis.

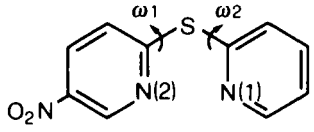

FIGURE 3 The NPTP molecule in the assumed N(1), N(2)-*inside* all-planar starting conformation ($\omega_1 = \omega_2 = 0°$). In the numbering scheme of *A* (Figure 1) positive angles ω_1 and ω_2 are described by clockwise rotation of the planes N(1)–C(5)–S(1) and C(5)–S(1)–C(6), respectively. This convention for rotations is adopted for definition of ω_1, ω_2 in X-ray and dipole moment analyses as well as in theoretical calculations.

local minimum zone. The geometries attained for the optimized structures and the solid-state ones were comparable.

RESULTS AND DISCUSSION

Crystal Structure Determination and Theoretical Calculations

The compound crystallizes with two independent molecules per asymmetric unit, as reported for the parent compound 2,4-dinitro-diphenylsulphide.[15] Hereafter, these molecules will be referred to as *A* and *B*. The two independent molecules *A* and *B* are closely similar as regards their bond lengths and angles (Table II). In particular, the length of the C–S bonds (mean value of 1.770(7) Å) corresponds closely to that expected for a single bond between S and sp^2 hybridized carbon atom and it compares well with those found earlier in six symmetric diphenylsulfide derivatives (mean: 1.780(6) Å)[16–21] and in ten unsymmetrically substituted diphenylsulfides (mean: 1.776(4) Å).[15,22–27]

The NPTP, in both *A* and *B* independent molecules, adopts a twisted conformation in which the relative orientations of the pyridine nitrogen atoms N(1) and N(2) with respect to the C–S–C angle are N(1), N(2)-*outside* (*A*) and N(1)-*inside*/N(2)-*outside* (*B*). In molecule *A*, the nitro-substituted and unsubstituted pyridine rings deviate from coplanarity with C–S–C plane by the angles values 12.5° and 41.7°, respectively. In *B* the former angle is almost unchanged (12.1°), whereas the latter is raised up to 59.7°. The O_2N–C_5H_3N–S– fragment thus adopts the same slightly twisted (by ~12°) N-*outside* arrangement in both molecules, the conformational difference between *A* and *B* being determined by the two possible separate orientations N-*inside* and N-*outside* assumed by the –S–C_5H_4N moiety. By assuming that intermolecular packing forces in the crystal are not conformation determining factors, the above occurrence as well as the larger twisting angles (59.7° and 41.7°) can be reasonably accounted for by expectable lower double-bond character of the S–C(6) bond and by interatomic repulsion effects for pyridine rings predominantly steric in nature.

The symmetric and unsymmetric diphenylsulfide derivatives most frequently assumed the similar skew conformation. As reported for (4-nitrophenyl)phenylsulfide and (4-nitrophenyl)(4-dimethylaminophenyl)sulfide,[24] being also in the present compound the 5-nitropyridine ring virtually almost coplanar with C-S-C central plane, π-interactions in the solid appear to manifest themselves only as sulfur pπ-donations towards aromatic rings carrying strongly electron-withdrawing substituents.

However, the following feature in *A* and *B* is different: the two torsion angles involved in the N–C–S–C–N fragment (ω_1 and ω_2 of Table III) are −167.9°, −138.3° for *A* and 167.5°, 59.7 for *B*. This implies that the N · · · N contact is 5.03 Å in *A* and 4.55 Å in *B*.

The molecular packing in the crystal (Figure 2) can be thought of as governed by van der Waals interactions and there are no intermolecular short contacts in the structure, even if the two indipendent molecules have somewhat short contacts (3.19; 3.30; 3.32 Å) between nitrogroups and the aromatic rings of neighbouring molecules, as yet observed in 2,4-dinitrodiphenylsulfide.[15]

The calculated conformational energy map is shown in Figure 4, in which two symmetric minima were located at $\omega_1 = 36°$, $\omega_2 = 54°$ and $\omega_1 = -36°$, $\omega_2 = -54°$. These two minima correspond to a single preferred conformation N(1), N(2)-*inside* in which the 5-nitropyridine ring is rotated out of the coplanar arrangement with the C(5)–S–C(6) plane by a smaller degree (36°) than the pyridine ring (54°). The AM-1 calculation gives a preference for this conformation mainly because of steric reasons. The less twisted arrangement of the 5-nitrosubstituted ring in the solid was therefore found energetically unfavourable for the isolated molecule. While being aware that there is no necessary correlation between crystal structure and gas phase conformation, the comparison shows that in both conformations *A* and *B* of the solid, by contrast with theoretical results, the 5-nitropyridine ring is not only close to coplanarity with C(5)–S–C(6) atoms but it is also N(2)-*outside* orientated.

From Figure 4 it is of interest to get information about the molecular flexibility of NPTP. The calculated rotational barrier about C(5)–S and C(6)–S bonds are 4–5 kcal mol^{-1}, for which essentially free rotation as well as interconversion

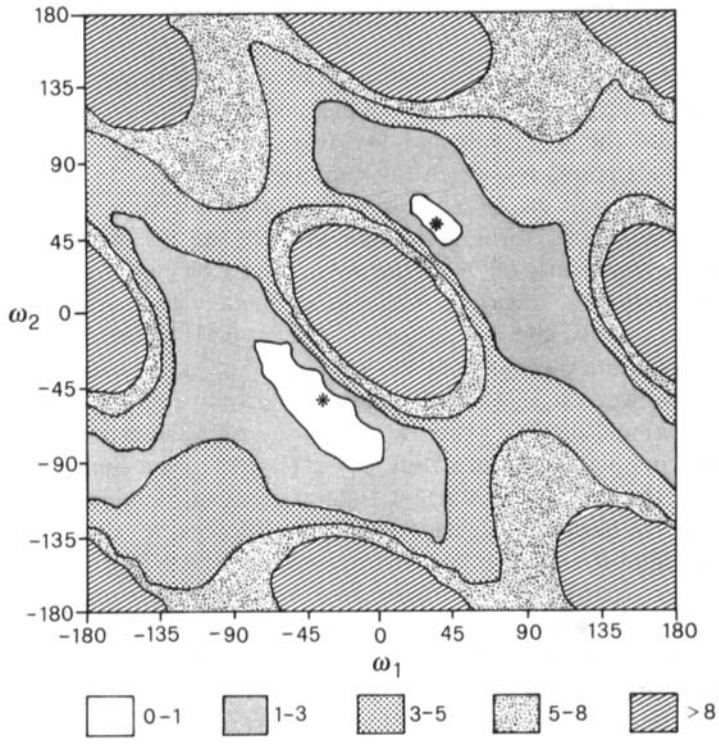

FIGURE 4 Conformational map for NPTP. The absolute minima are denoted by the asterisks. All energies are reported in kcal mol^{-1}, relative to the zero-energy conformation.

processes among the two "conformational enantiomers" are unlikely. The conformational map (Figure 4) also indicates that some torsional oscillations about these bonds are energetically possible about the minimum energy conformations.

Dipole Moment Analysis

A three-dimensional vector addition method of component group moments was used to obtain the resultant calculated μ values (μ_{calcd}) for the possible conformations of NPTP denoted by ω_1, ω_2 angles (Figure 3). The group moment of the $-S-C_5H_3N-NO_2$ portion was evaluated by combining the moment of pyridine (2.20 D)[28] with that of the $-S-C_6H_4-NO_2$ fragment (2.77 D) as deduced from the μ_{exp} of the disulphide $(C_6H_4-NO_2)_2S_2$ (4.31 D);[29] the group moment of the $-S-C_5H_4N$ half-molecule was estimated by combination of the experimental moments of pyridine with that of the $-S-C_6H_5$ moiety (1.29 D) as calculated from the μ_{exp} of diphenylsulphide $(C_6H_5)_2S$ (1.55 D).[30] The sulphur valency angle of NPTP was assumed fixed at the average value (106°) of molecules *A* and *B* in the solid.

Rotations in the whole ω_1, ω_2 ranges (from 0° to 180°, because of the molecular symmetry) caused significant changes in the μ_{calcd} values (from 0.9 D for $\omega_1 = \omega_2 = 0°$ to 5.6 D for $\omega_1 = \omega_2 = 180°$) the difference thus being suitable to

provide conformational information by the comparison of μ_{exp} (4.84 D) with μ_{calcd} as a function of ω_1, ω_2.

The possibility of occurrence in solution of the energetically favoured conformation could initially be excluded on the basis of the significantly large difference between μ_{exp} and the μ_{calcd} value (3.08 D) for $\omega_1 = 36°$, $\omega_2 = 54°$. The contour which connects all points for which the condition $\mu_{calcd} = \mu_{exp}$ is verified showed that there are numerous ω_1, ω_2 combinations compatible with the μ_{exp} value.

However, on the basis of the good agreement of the μ_{exp} with the μ_{calcd} value (4.97 D) for the conformation *A* of the solid, it can be reasonably inferred that such a conformation is retained in the fluid, namely the $\omega_1 = -167.9°$, $\omega_2 = -138.3°$ (or, as it is the same, $\omega_1 = 12°$, $\omega_2 = 41.7°$). Occurrence of the conformation of the molecule *B* of the crystal in solution seems unlikely, being the difference between μ_{calcd} (5.22 D) and μ_{exp}, less close to the limit of accuracy of the dipole moment method. Therefore the μ_{exp} can be interpreted in terms of a predominantly populated conformation of NPTP in solution similar to that of the molecule *A* of the crystal. This result suggests that intramolecular interactions, more than intermolecular effects and packing forces in the crystal, should determine the almost skewed conformation adopted by NPTP in both solid and solute states. In particular, in these two states of aggregation a common equilibrium ratio between electronic and steric effects should determine and stabilize the NPTP conformation. In all cases, the relative difference between ω_1 and ω_2 values appears significant in that reflects electronic effects due to the 5-nitro group, which, through π-delocalization, push the NO_2-bearing ring towards a smaller ω_1 twisting angle.

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