π-Bond Anisotropy and C—D···O Hydrogen Bonding in the Crystal Structure of Deuterionitromethane
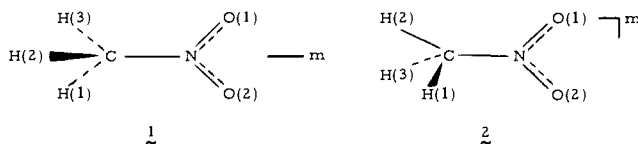
G. A. Jeffrey,*† J. R. Ruble,† L. M. Wingert,† J. H. Yates,†§ and R. K. McMullan‡

Contribution from the Department of Crystallography, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, and the Department of Chemistry, Brookhaven National Labortory, Upton, New York 11973. Received March 19, 1985

Abstract: The crystal structure of deuterionitromethane has been refined using single crystal neutron diffraction data at 15 K. The conformation of the molecule is such that the N–C–D(2) plane makes an angle of 89.7 (1)° to the mean CNO_2 plane. The N atom is displaced by 0.0112 (7) Å out of the carbon and oxygen plane, trans to the C–D(2) bond. This nitrogen pyramidalization is reproduced in magnitude and direction by ab initio molecular orbital calculations for the isolated molecule at the HF/3-21G, 6-31G, and 6-31G* approximation levels. This crystal structure analysis confirms an earlier report based on neutron powder diffraction data that the two N–O bond lengths are different, but reverses the sense of the difference. The N–O bond, which is longer by 0.0045 (15) Å, has four intermolecular O···D distances ranging from 2.39 to 2.58 Å, which qualify as C—D···O hydrogen bonds. The oxygen of the shorter N–O bond has five deuterium neighbors at longer distances ranging from 2.69 to 3.09 Å.

The reported crystal structure of nitromethane[1] has several unusual features. The observed molecular conformation is that having approximate *m* symmetry, as shown by conformer **1**, yet the two N–O bond lengths are unequal. The structure refinements were based on two independent experiments. One was an X-ray single crystal structure analysis at 228 K, which is 17 K below the melting point. The other was by neutron diffraction using the powder method and profile analysis of deuterionitromethane at 4.2 and 78 K. In the single crystal analysis, N–O(1) > N–O(2) by 0.018 (5) Å, but in the neutron analyses, N–O(1) < N–O(2) by 0.014 (7) and 0.023 (10) Å.[2] Another interesting feature of the crystal structure is that the two oxygen atoms have different crystal field environments. Oxygen O(1) has four nearest deuterium intermolecular neighbors at distances ranging from 2.39 to 2.58 Å, whereas O(2) has five deuterium neighbors at longer distances ranging from 2.69 to 3.09 Å. There is, therefore, a rationale for asymmetry in the NO bonds, but in the opposite direction to that observed in the previous neutron diffraction experiments.

A third interesting aspect of the nitromethane structure is the conformational similarity of the molecule to acetamide in its rhombohedral crystal form,[3] and to one of the two different conformers in the crystal structure of thioacetamide.[4] In all three structures, the orientation of the methyl group is that in conformer **1**. In acetamide and thioacetamide, this methyl group conformation is associated with a distortion from planarity of the sp^2 carbon atoms. This π-bond anisotropy, or pyramidalization, which is small, <2°, is also observed at the nitrogen atom in the nitromethane structure in both the X-ray single crystal and the neutron powder diffraction analyses, and in the crystal structure of the complex, $2CH_3NO_2 \cdot K_2Co(NCS)_4 \cdot H_2O$.[5] Ab initio calculations[6] for the isolated nitromethane molecule at rest showed that at all levels of approximation studied, the two *m* symmetry conformers **1** and **2** had insignificant differences in energy. In

1, the N–O bonds are equal and the N is pyramidal by 1.7 to 2.1°, depending on the basis set used, thereby providing evidence that

Table I. Crystal Data for Deuterionitromethane

	powder data[a]		single crystal data 15 K
	4.2 K	78 K	
	space group $P2_12_12_1$		
a, Å	5.1832 (1)	5.1983 (3)	5.185 (1)
b, Å	6.2357 (2)	6.2457 (3)	6.237 (1)
c, Å	8.5181 (2)	8.5640 (4)	8.507 (2)
λ_n, Å	1.541	1.541	1.0505 (2)
D_c, mg/m³	1.545	1.533	1.547

[a] Reference 1.

the pyramidalization is a molecular property, rather than a consequence of crystal field forces. In **2**, the calculated N–O bond lengths are unequal, and the $C-NO_2$ group is exactly planar. Because the structural differences of chemical interest are small, we have obtained more definitive experimental evidence relating to these features from single crystal neutron diffraction data obtained with deuterionitromethane at 15 K.

Experimental Section

The single crystal neutron diffraction data collection at the Brookhaven High Flux Beam Reactor followed the same procedures as previously described for thioacetamide,[4] except for the information provided below.

The crystal was grown from the liquid in a glass capillary into which a Pt pin was inserted. The Pt pin was mounted in a Cu rod which was cooled by lowering into liquid nitrogen. The capillary was heated by two infrared lamps, which were controlled so as to cause the temperature to fall with an oscillating mode. This melted any superficial small crystals and consolidated the main crystal that grew on the Pt pin. The capillary and Pt pin were transferred to the cold finger of a DISPLEX cryostat, using a movable cold-box maintained at −50 °C which could be placed close to the neutron diffractometer. A transparent specimen 0.35 cm in length and width proved to be two crystals, the smaller of which could be more readily centered in the beam. The orientation of both crystals was determined by searching for the stronger reflections calculated from the

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†University of Pittsburgh: Research Collaborators at Brookhaven National Laboratory, which is operated under contract with the U. S. Department of Energy.

‡Brookhaven National Laboratory.

§Present address: Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104

Table II. Atomic Coordinates ($\times 10^5$) and Anisotropic Thermal Parameters ($\times 10^4$) for Deuterionitromethane at 15 K[a]

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C	13 388 (14)	105 522 (11)	37 628 (9)	59 (3)	74 (3)	103 (3)	15 (2)	−5 (2)	−5 (2)
N	36 298 (10)	91 224 (8)	37 443 (5)	47 (2)	55 (2)	74 (2)	6 (2)	2 (2)	0 (2)
O(1)	51 929 (18)	92 771 (14)	48 212 (10)	64 (3)	91 (3)	100 (3)	8 (3)	−21 (3)	1 (3)
O(2)	38 188 (18)	78 235 (14)	26 742 (10)	93 (3)	84 (3)	108 (3)	12 (3)	3 (3)	−37 (3)
D(1)	7 526 (28)	108 050 (25)	25 649 (12)	353 (6)	439 (7)	185 (4)	234 (6)	−87 (4)	−17 (5)
D(2)	−1 308 (24)	97 179 (22)	44 080 (20)	184 (5)	259 (5)	610 (8)	46 (4)	190 (5)	149 (5)
D(3)	18 570 (24)	120 212 (18)	43 407 (17)	229 (5)	165 (4)	461 (6)	50 (4)	−84 (5)	−145 (4)

[a] Isotropic secondary extinction parameter for type 1 crystal with Lorentzian distribution;[8] $g = 0.1286$ (85) $\times 10^4$ rad^{-1}.

Table III. Experimental Molecular Dimensions for CD_3NO_2 at 15 K[a]

Valence Angles (deg)			
C–N–O(1)	118.2 (1)	N–C–D(1)	107.7 (1)
C–N–O(2)	118.0 (1)	N–C–D(2)	106.4 (1)
O(1)–N–O(2)	123.7 (1)	N–C–D(3)	108.5 (1)
Torsion Angles (deg)			
O(1)–N–C–D(1)	151.7 (1)	O(2)–N–C–D(1)	−29.9 (1)
O(1)–N–C–D(2)	−89.4 (1)	O(2)–N–C–D(2)	88.9 (1)
O(1)–N–C–D(3)	29.9 (1)	O(2)–N–C–D(3)	−151.7 (1)

[a] The bond lengths are given in Table IV.
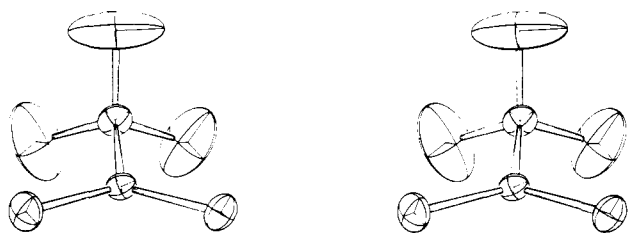
Figure 1. The molecular structure of deuterionitromethane at 15 K. The thermal ellipsoids are plotted at 75% probability.

previous 78 K structure analysis.[1] The lattice parameters given in Table I were obtained from the 2θ values of 16 Friedel pairs of intense reflections, with $50 \leq 2\theta \leq 57°$, and h, k, and l indices in approximately the same proportion as the corresponding lattice dimensions. Intensities in two equivalent octants, hkl and $\bar{h}kl$, were collected at a rate of about 20 reflections per hour. The scan profile data were plotted for each recorded reflection. From these and orientation matrices of both crystals, those reflections where there was overlap were identified and removed from the refinement data. The agreement factor $R(F_o^2)$ between the data for 502 pairs of symmetry equivalent reflections was 0.018.

The structure refinement, using the program UPALS,[7] was carried out with an assumed $\bar{T} = 0.25$ cm and with an isotropic extinction parameter on 641 reflections, minimizing $\sum w(F_o^2 - F_c^2)$, where $w = [\sigma^2(F_o^2) + (0.02 F_o^2)^2 + (K/F_o^2)^2]^{-1/2}$. A value of $K = 4791$ was obtained so that $\sigma(F_o^2) = F_o^2$ for those reflections where the space group requires $F_c = 0$. Zero weight was given to five reflections for which extinction was severe. The extinction corrections for the included reflections were $<1.35 F_o^2$. The final agreement factors were $R(F^2) = 0.036$, $wR(F^2) = 0.053$, $S = 1.87$.

The atomic parameters are given in Table II, the corresponding molecular dimensions in Tables III and IV. Figure 1 shows a stereo OR-TEP[9] of the thermal ellipsoids at 75% probability. As in acetamide and thioacetamide, those of the deuteriomethyl group are elongated perpendicular to the C–D bonds.

Comparison with Previous Results

The comparison of these results with those reported previously for the covalent bond lengths is given in Table IV. The only significant difference between the neutron powder result at 4.2 K and the neutron single crystal result is the 0.018 Å (4.5σ) in the N–O(1) bond length. The accuracy of the standard deviations derived from powder profile diffraction analysis is presently

Table IV. Bond Lengths: Comparison with Previous Results

	X-ray single crystal, 228 K	neutron powder profile refinement		neutron single crystal, this work, 15 K
		78 K	4.2 K	
C–N	1.448 (5)	1.489 (5)[a]	1.481 (3)	1.4855 (9)
N–O(1)	1.231 (4)	1.203 (7)[b]	1.209 (4)	1.2270 (9)
N–O(2)	1.213 (4)	1.226 (7)	1.223 (4)	1.2225 (9)
C–D(1)		1.000 (8)[a]	1.074 (4)	1.0751 (13)
C–D(2)		1.001 (6)[a]	1.074 (3)	1.0736 (14)
C–D(3)		1.001 (7)[a]	1.075 (3)	1.0739 (13)

[a] These bond lengths are obtained by assuming a transcription error in the carbon z coordinate to read 0.3793 in Table II of the original paper. The C–D bond lengths in Table III include thermal motion corrections and are longer than those given above. [b] Assuming no other errors in Table II of the original paper, this bond length was calculated incorrectly for Table III.

Table V. Rigid Body Motion of the CNO_2 Segment with Respect to the Inertial Axes About the Center of Mass

	I_1, deg	I_2, deg	I_3, deg
T, Å	0.079	81.3	164.3	102.9
	0.075	66.7	74.5	151.5
	0.065	25.1	87.3	65.1
ω, deg	4.0	33.7	68.4	114.5
	2.3	69.0	76.3	24.9
	2.0	64.4	154.0	86.1

controversial.[10] The discrepancy of 0.04 Å (8σ) in the C–N bond between the 228 K X-ray result and the 15 K neutron analysis can be explained, at least in part, by the shortening effect due to greater thermal oscillation at the higher temperature.[11] In the N–O bonds, this shortening effect may be compensated, in part, by the distribution of the electron densities, the peaks of which may not coincide with the oxygen nuclear positions given by the neutron diffraction analyses.

It is relevant to note, however, that the results of the two single crystal refinements were not significantly different. The two features of particular chemical interest were retained in the neutron refinement which gave N–O(1) > N–O(2) by 0.0045 (15) Å and a nitrogen pyramidalization of 1.48 (9)°.

Thermal Motion Analysis

Thermal librational motion will result in observed bond lengths which are shorter than those calculated for the molecule *at rest*. Although these effects are small, they are significant in terms of the experimental precision, even at 15 K. Differences in the thermal motion of the two oxygen atoms could therefore result in differences in N–O bond lengths of the order of magnitude observed. A thermal motion analysis was therefore carried out to compare the results more directly with the theoretical calculations of the molecular structure, at rest. Since standard rigid-body analysis, which includes all four nonhydrogen atoms, led to a singularity, the segmented-body analysis method[12] was applied. The segments used were CNO_2 and CD_3. For the C–D bonds

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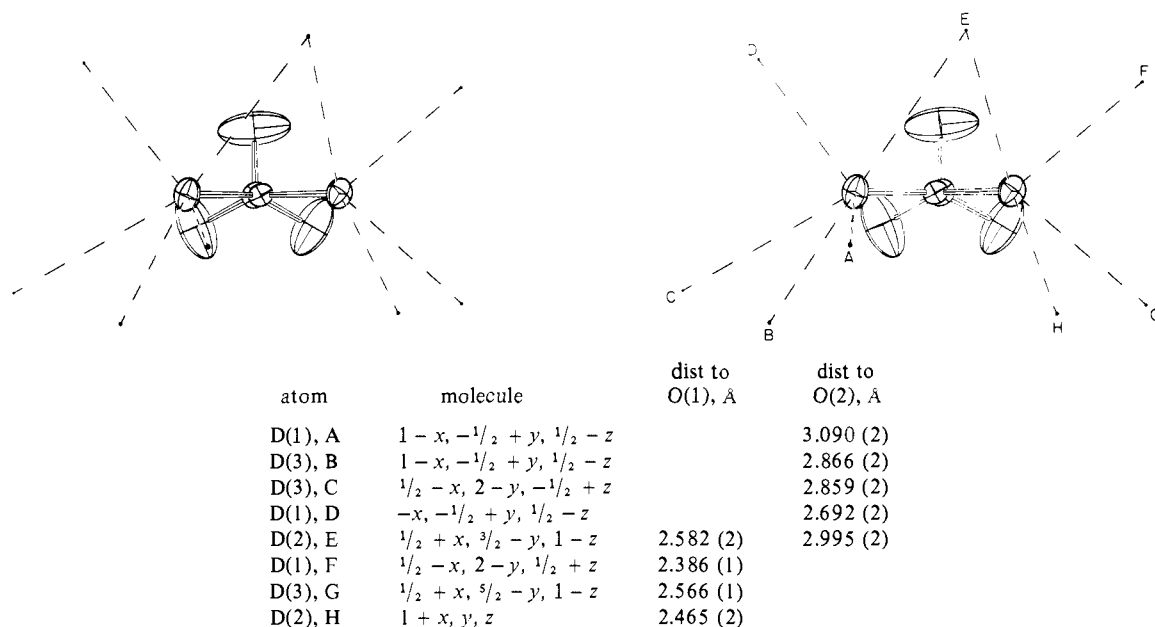(10) Scott, H. G.; *J. Appl. Crystallogr.* **1983**, *16*, 159–163.

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Table VI. Ab Initio Geometries of the Nitromethane Conformers "at Rest" vs. Experimental Values with Bond Lengths Corrected for Thermal Motion

	conformer **1**			conformer **2**			
	3-21G	6-31G	6-31G*	3-21G	6-31G	6-31G*	exptl values
C–N^a	1.493	1.479	1.478	1.493	1.479	1.479	1.488
N–O(1)	1.240	1.222	1.192	1.239	1.221	1.191	1.231
N–O(2)	1.240	1.222	1.192	1.242	1.223	1.193	1.225
C–D(2)	1.080	1.079	1.080	1.073	1.073	1.076	1.093
C–D(1)	1.074	1.074	1.076	1.078	1.077	1.079	1.092
C–D(3)	1.074	1.074	1.076	1.078	1.077	1.079	1.091
O(1)–N–C–D(2)^b	−88.9	−89.1	−89.1	0.0	0.0	0.0	−89.4 (1)
⊥N^c	+0.0163	+0.0126	+0.0122	0.0	0.0	0.0	+0.0112 (7)
$\langle \theta_p N \rangle^d$	2.14	1.68	1.66	0.0	0.0	0.0	1.48 (9)

^{a} Bond lengths are in Å. ^{b} Torsion angles are in degrees. ^{c} ⊥N is the displacement (in Å) of the N atom from the carbon–oxygen plane with the positive direction trans to C–D(2). ^{d} $\langle \theta_p N \rangle$ is the average pyramidalization (in deg) of the bonds ($\vec{V}_i$, $\vec{V}_j$, and $\vec{V}_k$) from N. $\theta_p = \cos^{-1}[\vec{V}_i \cdot (\vec{V}_j \times \vec{V}_k)/|\vec{V}_i||\vec{V}_j \times \vec{V}_k|] - 90°$. The C–D distances include an anharmonic correction of $-\frac{3}{2}a(U_D{}^{\parallel} - U_C{}^{\parallel})^2$ where $U_D{}^{\parallel}$ and $U_C{}^{\parallel}$ are the components of the anisotropic temperature factors parallel to the C–D bonds, and $a = 1.98$.

atom	molecule	dist to O(1), Å	dist to O(2), Å
D(1), A	$1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$		3.090 (2)
D(3), B	$1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$		2.866 (2)
D(3), C	$\frac{1}{2} - x, 2 - y, -\frac{1}{2} + z$		2.859 (2)
D(1), D	$-x, -\frac{1}{2} + y, \frac{1}{2} - z$		2.692 (2)
D(2), E	$\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$	2.582 (2)	2.995 (2)
D(1), F	$\frac{1}{2} - x, 2 - y, \frac{1}{2} + z$	2.386 (1)	
D(3), G	$\frac{1}{2} + x, \frac{5}{2} - y, 1 - z$	2.566 (1)	
D(2), H	$1 + x, y, z$	2.465 (2)	

Figure 2. Intermolecular environment of the nitro oxygens O(1) and O(2), with thermal ellipsoids at 75% probability.

an internal root mean square (rms) stretch correction of 0.066 Å and a rms inward bending of 0.105 Å were assumed.[13] These values were those used in the neutron diffraction analysis of acetamide at 23 K.[3] With these motions subtracted, the least-squares rigid-body analysis of the CNO_2 group gave good overall fits with rms $\langle U_{ij}{}^{obsd} - U_{ij}{}^{calcd} \rangle = 0.0005$ Å^2, $\sigma(U_{ij}) = 0.0007$ Å^2. The corresponding rms torsion of the CD_3 group was 12.3°. The results of the thermal motion analysis are given in Table V.

Ab Initio MO Calculations

The fully optimized structure of nitromethane in conformation **2** was previously calculated at the Hartree–Fock level with 3-21G, 6-31G, and 6-31G* basis sets, while that of conformer **1** was only available with the 3-21G basis.[14] The corresponding higher level calculations were completed using GAUSSIAN 82,[6] giving the results shown in Tables VI and VII. At all levels of approximation, the energies of the two conformers are not significantly different. Almost free rotation of the methyl group must therefore take place in the liquid state from which the crystals were grown.

The agreement between the calculated and the experimental thermally corrected bond lengths shown in Table VI is comparable with that obtained for other first-row element molecules in similar comparative experiments.[15] The addition of the polarization

functions in the 6-31G* basis had no significant effect on the C–N bond length, but adversely affected the agreement for the N–O bonds. As in other comparisons of low-temperature neutron diffraction analyses with theoretical calculations, the agreement in the C–D bond lengths is better if no corrections are made for thermal motion.[15] This is because the bond shortening due to the riding motion and the bond lengthening due to anharmonicity[16] tend to cancel at ∼10 K.[17,18] In this analysis, the calculated C–D bond lengths are 0.012 to 0.020 Å shorter than the thermally corrected observed values. While this is consistent with the effect of the C—D···O hydrogen bonding, postulated later, it could also be due to an underestimation of the anharmonicity correction. The valence angles were insensitive to basis set, and in good agreement with the experimental values, e.g., C–N–O = 117.8° (theory), 118.1° (exptl).

CD···O Hydrogen Bonding in Deuterionitromethane

The spectroscopic evidence for the existence of CH···O intermolecular hydrogen bonding between appropriate molecules is long standing,[19] while the crystallographic evidence has been controversial.[20] It has recently been reviewed,[21] with the con-

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Table VII. Calculated Energies of Nitromethane Conformers[a]

	basis set		
	3-21G	6-31G	6-31G*
conformer 1	-242.25586	-243.52645	-243.66199
conformer 2	-242.25585	-243.52643	-243.66198
$E(1) - E(2)$[b]	-0.026	-0.060	-0.026

[a] Energy values in hartrees. [b] These differences (in kJ/mol) are not significant; the conformers are essentially equal in energy at the three levels of theory.

clusion that C–H intermolecular contacts to carbonyl oxygens are significantly shorter relative to the van der Waals radius sums than are those to carbon or hydrogen atoms. In that analysis, an H⋯O separation of 2.70 Å was used as the arbitrary criterion against which the observed distances were compared. With the same criterion, O(1) in the nitromethane structure receives four hydrogen bonds with D⋯O distances 2.39 to 2.58 Å, while O(2) receives none, with the shortest D–O distances ranging from 2.69 to 3.09 Å. Whether these interactions are referred to as hydrogen bonds or van der Waals interactions, the intermolecular environment of O(1) is significantly different from that of O(2), as shown in Figure 2. The fact that the calculated energies of conformers 1 and 2 are almost equal suggests that the CD⋯O interactions play a significant role in determining which of the two nitromethane conformers occurs in the crystalline state.

Strong H⋯O hydrogen bonding is known from experimental data on formic, acetic, and propionic acid monomers and dimers to lengthen the C=O bonds.[22] Similar results have been obtained from theoretical calculations on formamide monomers and hydrogen-bonded dimers.[23] The observed difference in the N–O bonds of 0.0045 (15) Å in the crystal structure of nitromethane is significant[24] and consistent with the concept that O(1) has a stronger CD⋯O hydrogen-bonding environment than O(2). This is the first time that the CD⋯O hydrogen bonding has been correlated with differences between the structure of the isolated molecule and that of the molecule in the crystal.

π-Bond Anisotropy in Deuterionitromethane

Small departures from planarity of the bonds from sp^2 carbon atoms have been observed in the precise low-temperature single crystal neutron diffraction analyses of acetamide[3] and thioacet-amide.[4] In both analyses, the conformers in which this nonplanarity is observed are asymmetric with respect to the symmetry plane of the C=O or C=S π-bonding. In acetamide, one of the CCH planes is at 86.7 (2)° to the π-bond plane, and the displacement of the carbonyl carbon atom from the plane is trans to the CH bond, with pyramidalization of 1.50 (14)°. In thioacetamide, there are two symmetry-independent molecules. In one, the molecule is asymmetric with a CCH plane at 75.6 (1)° to the nonhydrogen atom mean plane, and a smaller pyramidalization of 0.60 (8)° is observed. In both these molecules, the pyramidalization of the sp^2 carbon atoms is reproduced in magnitude and direction by ab initio calculations, indicating that these are intrinsic molecular properties of the isolated molecules, rather than crystal field effects.

In the structure of nitromethane, the same effect is observed with respect to the sp^2 N atom of the nitro group. The nitrogen atom is displaced 0.0112 (7) Å out of the plane of the carbon and oxygen atoms in the direction trans to the C–D(2) bond. This corresponds to a pyramidalization, θ_p, value of 1.48 (9)°. In consequence, the O–N–C–D(2) torsion angles are both less than 90.0°.

In the crystal structure of $2CH_3NO_2 \cdot K_2Co(SCS)_4 \cdot H_2O$, the nitromethane molecule is also in conformation 1, having an N–C–H plane at 84.9 (3)° to the mean CNO₂ plane. The pyramidalization at the nitrogen atom is $\theta_p = 0.96$ (11)° with the nitrogen 0.0073 (13) Å out of the plane of the carbon and oxygen atoms. In this structure, the two N–O bond lengths are equal, 1.222 (1) and 1.223 (1) Å.

Pyramidalization is also reproduced by the ab initio calculations on the isolated molecule, at all levels of approximation, shown in Table VI. Hitherto, the theoretical and experimental studies of π-bond anisotropy have been concerned with alkenes and carbonyls.[25,26] These are the first examples reported involving the nitrogen atom of a nitro group.

Supplementary Material Available: Tables of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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