

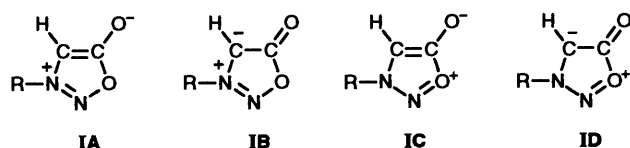
Theoretical Studies on the Structure and Electronic Properties of 3-(4-Tolyl)sydnone

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The structure of 3-(4-tolyl)sydnone has been calculated using the semiempirical MNDO, AM1 and PM3 methods and at the *ab initio* STO-3G, 3-21G and 6-31G** levels and the resulting geometries compared and contrasted with the well resolved crystal structure. While the geometry of the phenyl ring is well reproduced particularly by the *ab initio* methods, none of the methods give a satisfactory account of the geometry of the sydnone ring. The calculated charge distributions of atoms in the heterocyclic ring vary considerably depending on both the molecular orbital method used and the analysis technique adopted. The calculated dipole moments are generally overestimated with the best results obtained with the MNDO method for the semiempirical procedures and the STO-3G basis set for the *ab initio* methods.

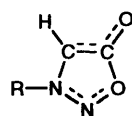
A considerable effort has been expended on the elucidation of the electronic structure of the sydnones (**I**) since their discovery in 1935.¹ In the most popular representation of their unique meso-ionic structure, the π -electrons are partitioned among the constituent atoms so that either one of the nitrogen atoms or the ring oxygen is positively charged with the carbonyl oxygen or a ring carbon negatively charged^{2,3} as shown in the canonical forms illustrated (Scheme 1). These structures are supported by



Scheme 1 Resonance forms of sydnone (**I**)

the fairly substantial experimental dipole moments of around 7 D for many 3-substituted derivatives.³

Theoretically, the electronic properties of the sydnones such as 3-methylsydnone (**Ia**), have been calculated at a number of



- I a** R = Me
b R = 4-MeC₆H₄-
c R = 4-EtOC₆H₄-
d R = 4-PrⁱOC₆H₄-
e R = 4-BrC₆H₄-
f R = 2-NH₂C₆H₄-

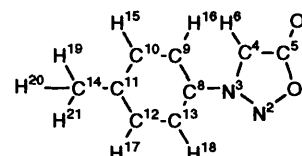
levels which include extended Huckel theory,⁴ the semiempirical CNDO/2 method⁵ and a restricted *ab initio* treatment.⁶ More recently, structural calculations have been reported on 3-methylsydnone (**Ia**) at the 6-31G level with a bonding analysis carried out using a molecular orbital valence bond approach.⁷ None of the methods, however, appear to give a good account of the meso-ionic character of the sydnones, and furthermore, little or no attempt has been made to relate the calculated structures obtained using different basis sets to data available from experimental sources.

In the present studies, calculations have been carried out at different levels of theory to probe the structure, conformation and electronic properties of 3-(4-tolyl)sydnone (**Ib**), a molecule

which has been extensively studied both by crystallography and by determination of its molecular dipole moment.

Methods of Calculation

Molecular orbital calculations were carried out on an empirical structure for 3-(4-tolyl)sydnone (**Ib**) using the MNDO,⁸ AM1⁹ and PM3¹⁰ methods of the MOPAC program¹¹ and the STO3G, 3-21G and 6-31G** basis sets¹² of the GAMESS program¹³ with full optimization of all bond lengths, angles and torsion angles. The numbering convention adopted for each atom in these studies is shown in Scheme 2.



Scheme 2 Numbering convention adopted for the 3-(4-tolyl)sydnone (**Ib**)

Discussion

Experimental Structures.—An examination of the Cambridge Structural Database¹⁴ shows the presence of a number of 3-substituted sydnones including the 4-tolyl- (**Ib**),¹⁵ 4-ethoxyphenyl- (**Ic**),¹⁵ 4-isopropoxyphenyl- (**Id**),¹⁶ 4-bromophenyl- (**Ie**)¹⁷ and 2-aminophenyl- (**If**)¹⁸ derivatives. In most of these examples, the heterocyclic ring is essentially planar with a characteristic C=O bond length of 1.21–1.22 Å (Table 1) and internal bond lengths of 1.38 (O1–N2), 1.31 (N2–N3), 1.32–1.34 (N3–C4), 1.39–1.40 (C4–C5) and 1.39–1.42 Å (O1–C5). However, the phenyl group of the molecule is twisted around the N–phenyl bond in some of the examples, but not in others. For example, while the torsion angle of the phenyl carbon at the C9 position (C4–N3–C8–C9) is 36 and 26.9° below the plane of the sydnone ring in the 4-tolyl- (**Ib**) and the 4'-bromophenyl- (**Ie**) derivatives respectively, that in the 4'-isopropoxyphenyl-derivative (**Id**) is twisted 24° above the plane of the sydnone ring (Table 1).

In contrast, the two aromatic rings are almost co-planar in the 4'-ethoxyphenyl- derivative (**Ic**) with the same torsion angle at C9 of only 0.7°. A similar effect is found in the 2'-aminophenyl- derivative (**If**), though here there are two molecules in the unit cell, one of which is almost planar with a torsion angle of 6.4° at the C9 position of the phenyl ring, whilst

Table 1 Crystallographic data for 3-phenylsydnones taken from the Cambridge structural database¹⁴

Parameter ^a	Ib ¹⁵ CIHGOP	Ic ¹⁵ CIHGJ	Id ¹⁶ DETOX	Ie ¹⁷ BROPSY	If ¹⁸ APHSYD ^b	
O1-N2	1.384	1.385	1.384	1.365	1.381	1.386
N2-N3	1.314	1.307	1.315	1.336	1.312	1.312
N3-C4	1.329	1.329	1.333	1.379	1.338	1.321
C4-C5	1.404	1.402	1.400	1.411	1.389	1.394
C4-H6	0.995	1.061	1.013	1.081	0.960	0.826
C5-O7	1.217	1.211	1.211	1.201	1.226	1.218
C5-O1	1.408	1.407	1.420	1.421	1.380	1.385
N3-C8	1.445	1.447	1.441	1.407	1.442	1.444
C8-C9	1.375	1.370	1.377	1.410	1.396	1.391
C8-C13	1.379	1.380	1.385	1.402	1.401	1.407
C9-C10	1.379	1.392	1.386	1.366	1.361	1.376
C10-C11	1.378	1.385	1.385	1.423	1.387	1.379
C11-C12	1.379	1.379	1.391	1.378	1.358	1.369
C12-C13	1.378	1.376	1.370	1.378	1.406	1.412
C11-X14	1.493	1.362	1.363	1.889	1.365	1.354
O1-N2-N3	103.0	103.5	103.5	104.2	104.0	103.5
N2-N3-C4	115.7	115.3	115.3	114.6	113.9	114.3
N3-C4-C5	106.6	106.8	107.0	104.8	106.8	107.5
C4-C5-O1	103.3	103.4	103.3	105.1	104.5	103.6
C5-O1-N2	111.4	110.9	110.9	111.3	110.9	111.1
C4-C5-O7	136.5	136.9	137.1	135.7	135.0	135.9
C5-C4-H6	127.8	130.0	131.8	128.5	130.7	129.0
C4-N3-C8	127.7	127.8	127.2	127.2	127.0	126.9
N3-C8-C9	119.5	119.6	118.4	118.8	116.7	116.9
C8-C9-C10	118.2	119.3	118.8	120.5	120.5	120.1
C9-C10-C11	121.9	119.4	120.1	119.0	119.6	118.9
C10-C11-C12	118.4	120.4	119.8	120.5	120.2	121.4
C11-C12-C13	121.2	120.3	120.6	120.9	122.4	121.9
C12-C13-C8	118.8	119.0	118.9	119.0	116.2	115.4
C13-C8-C9	121.5	121.6	121.9	120.4	121.1	122.4
C10-C11-X14	121.4	124.9	125.2	118.0	124.8 ^c	125.0 ^c
C4-N3-C8-C9 ^d	35.9	-0.7	-23.7	26.9	6.4	-28.9
<i>R</i> -factor ^e	0.031	0.032	0.041	0.082	0.062	0.062

^a Bond lengths are given in angstroms, angles in degrees. ^b There are two molecules in the unit cell. ^c R14 is joined at position 13 in this case (Scheme 2) with modified angle C8-C13-NH₂. ^d Clockwise rotation from the sydnone ring; positive values are below the ring plane. ^e A measure of the agreement between the structure as postulated relative to the diffraction data as collected.

the other is twisted around the N-phenyl bond by 29° above the plane of the sydnone ring. These results suggest that the barrier to rotation in the 3-phenylsydnones is small though the N3-C8 bond length of 1.44 Å suggests that there is substantial overlap between the phenyl and sydnone rings.

Calculated Structures.—Calculations were carried out using both semiempirical and *ab initio* methods on 3-(4-tolyl)sydnone (**Ib**), which has the best resolved structure of those considered here (an *R*-factor of 3.1%, Table 1) and the results compared with and contrasted to the crystallographic data.

The calculations at both the MNDO⁸ and AM1⁹ level with full optimization of all geometric variables gives poor results with many bond lengths both overestimated and underestimated relative to the crystallographic data (Table 2). For example, both methods substantially underestimate the length of the O1-N2 bond giving values of 1.29 Å, in each case, *versus* 1.38 Å in the crystal. In contrast, the length of the N3-C4 bond is overestimated with values of 1.38 and 1.40 Å respectively *versus* 1.33 Å experimentally (Table 2), though the N2-N3 bond length is well reproduced at 1.31 Å. Surprisingly, the AM1 method gives an inferior result of 1.50 Å for the C5-O1 distance *versus* 1.42 Å for the MNDO method and 1.41 Å experimentally. The calculated angles show a better correlation with the crystallographic data in each case, but the O1-N2-N3 values in each case at 109° are overestimated *versus* the measured value of 103° (Table 2). The aromatic bond lengths in the phenyl ring are generally overestimated by both methods, often by a substantial

margin, though the internal angles show a reasonable correlation with experiment. Both methods predict a twist at the N-phenyl bond, with the AM1 method giving a torsion angle at C4-N3-C8-C9 of 34° *versus* 36° in the crystal and 68° by the MNDO method.

The PM3 method, in contrast, gives a slightly better description of the key bond lengths particularly for O1-N2 and C5-O1 with values of 1.40 Å in each case. However, the N3-C4 and C5-C4 distances and the O1-N2-N3 angle are overestimated, though the calculated torsion angle of the phenyl ring at 34° is close to the experimental value (Table 2).

The results obtained at the *ab initio* level are generally superior to those obtained at the semiempirical level as expected. At the STO-3G level, while the O1-N2 distance at 1.38 Å matches the experimental data (Table 2), the N2-N3 and C4-C5 bond lengths at 1.35 and 1.45 Å, are overestimated relative to the measured values of 1.31 and 1.40 Å respectively. The aromatic bond lengths at the phenyl ring, however, show a close fit with the crystallographic data. The internal angles of both the sydnone and phenyl rings show an excellent correlation with the experimental data with the values calculated for the heterocyclic ring showing a marked contrast to the results obtained at the semiempirical level (Table 2). Thus the calculated angles at the hetero-atoms of the sydnone ring of 104° (O1-N2-N3), 115° (N2-N3-C4), and 111° (C5-O1-N2) are almost identical with the measured values of 103°, 116° and 111°, respectively. The molecule is again predicted to be twisted

Table 2 Comparison between crystallographic data for 3-(4-tolyl)sydnone (**1b**) and that calculated by the MNDO, AM1, PM3 and *ab initio* STO-3G, 3-21G and 6-31G** methods^a

Parameter	X-ray ¹⁵	MNDO	AM1	PM3	STO-3G	3-21G	6-31G**
O1-N2	1.384	1.289	1.288	1.403	1.386	1.419	1.331
N2-N3	1.314	1.315	1.311	1.306	1.349	1.318	1.263
N3-C4	1.329	1.382	1.395	1.362	1.349	1.326	1.335
C4-C5	1.404	1.455	1.428	1.454	1.446	1.423	1.416
C4-H6	0.995	1.076	1.083	1.089	1.073	1.058	1.063
C5-O7	1.217	1.219	1.216	1.208	1.220	1.200	1.189
C5-O1	1.408	1.419	1.498	1.402	1.429	1.413	1.379
N3-C8	1.445	1.447	1.437	1.453	1.467	1.434	1.435
C8-C9	1.375	1.413	1.408	1.401	1.388	1.380	1.381
C8-C13	1.379	1.412	1.408	1.400	1.388	1.381	1.383
C9-C10	1.379	1.405	1.391	1.388	1.382	1.379	1.381
C10-C11	1.378	1.415	1.400	1.397	1.393	1.388	1.389
C11-C12	1.379	1.415	1.399	1.396	1.393	1.389	1.391
C12-C13	1.378	1.406	1.392	1.389	1.384	1.381	1.383
C11-C14	1.493	1.506	1.481	1.485	1.525	1.516	1.510
O1-N2-N3	103.0	109.0	108.7	107.9	104.0	102.6	105.4
N2-N3-C4	115.7	112.4	113.0	113.8	115.1	115.8	114.9
N3-C4-C5	106.6	103.7	105.7	104.5	106.0	107.6	105.3
C4-C5-O1	103.3	103.8	101.7	106.4	103.6	102.7	102.4
C5-O1-N2	111.4	111.1	110.9	107.5	111.3	111.3	112.2
C4-C5-O7	136.5	137.7	145.1	137.7	135.0	134.9	135.4
C5-C4-H6	127.8	130.6	129.7	127.7	130.9	128.7	131.0
C4-N3-C8	127.7	127.0	122.8	124.7	126.0	126.1	126.1
N3-C8-C9	119.5	119.3	119.5	119.3	119.1	119.3	118.7
C8-C9-C10	118.2	119.0	119.6	119.5	119.0	119.3	119.1
C9-C10-C11	121.9	121.5	120.8	120.5	121.0	121.0	121.2
C10-C11-C12	118.4	118.2	119.2	119.6	118.8	118.6	118.3
C11-C12-C13	121.2	121.5	121.0	120.7	121.1	121.1	121.5
C12-C13-C8	118.8	119.0	119.4	119.3	118.8	119.0	118.7
C13-C8-C9	121.5	120.8	120.0	120.5	121.3	121.0	121.2
C10-C11-C14	121.4	120.9	120.4	120.2	120.4	120.5	120.7
C4-N3-C8-C9 ^b	35.9	67.6	34.3	34.2	20.4	31.1	31.3
Dipole moment ^c	6.98 ^d 6.89 ^e	7.47	7.93	8.46	7.40	9.48	9.21
Total energy ^f					-596.3581	-600.5912	-604.000

^a Bond lengths are given in angstroms, angles in degrees. ^b Clockwise rotation from the sydnone ring; positive values are below the ring plane. ^c In Debyes. ^d Experimental data from ref. 22. ^e Experimental data from ref. 23. ^f In a.u.

around the N-phenyl bond with a torsion angle of 21° at C4-N3-C8-C9.

The results obtained at the 3-21G level show a marginally better correlation with the crystallographic data than those obtained with the STO-3G basis set though the O1-N2 and C4-C5 distances are overestimated at 1.42 Å in each case *versus* the experimental values of 1.38 and 1.40 Å respectively (Table 2). The calculated bond lengths of 1.32 and 1.33 Å at N2-N3 and N3-C4, however, are superior to those at the STO-3G level and show an excellent correlation with the experimental values of 1.31 and 1.33 Å respectively. All of the remaining bond lengths and angles show a very close correspondence with the experimental data. As in the previous cases, the sydnone is predicted to be twisted around the N-phenyl bond and the torsion angle of 31° at C4-N3-C8-C9 shows a good fit with the experimental value of 36° (Table 2).

Calculations at the 6-31G** level surprisingly show no real improvement over the 3-21G results, but for different reasons, with a number of important bond lengths predicted to be much shorter than those found in the crystal structure. For example, both the O1-N2 and N2-N3 bonds at 1.33 and 1.26 Å are far too short compared with the experimental values of 1.38 and 1.31 Å respectively. However, the other bond lengths in the phenyl ring and almost all the angles show an excellent correlation with the experimental data. On balance, the results obtained at this level of theory do not hold any advantage over the 3-21G results, despite the presence of many more basis

functions on each atom which would be expected to markedly improve the result.

Electronic Properties.—In terms of the calculated atomic charges, none of the theoretical methods support the resonance forms **1C** or **1D** of the sydnone (Scheme 1) as the ring oxygen, O1, is negatively charged in all cases (Table 3). However, there are considerable differences in the charges between the semiempirical and *ab initio* methods at other atoms. At the semiempirical level, the atomic charges are obtained simply from the calculated eigenvectors with neglect of the overlap integrals so that all of the electron population appears on the diagonal elements of the final density matrix. Using this approach, the ring nitrogen atom, N3, is positively charged and the ring carbon, C4, negatively charged with the PM3 method showing the largest charge separation. The PM3 charges strongly support the resonance structure **1B** and the bond lengths of 1.45 Å for C4-C5, 1.31 Å for N2-N3 and 1.21 Å for C5-O7 are consistent with the presence of one single and two double bonds, respectively. The AM1 and MNDO methods show similar charge distributions but the charge separation at the N3-C4 bond is much less pronounced. However, while the PM3 method gives a substantial negative charge at the bridgehead carbon of the phenyl ring, C8, the other methods show this atom to be broadly neutral.

The atomic charges calculated by the Mulliken population analysis¹⁹ for the *ab initio* methods, however, show completely different trends (Table 3) to the semiempirical methods. Here,

Table 3 Atomic charges in 4-tolylsydnone (**1b**) calculated by the MNDO, AM1, PM3 and *ab initio* STO-3G, 3-21G and 6-31G** methods

Atom	MNDO	AM1	PM3	Mulliken			Lowdin	DMA ^a
				STO-3G	3-21G	6-31G**	6-31G**	6-31G**
O1	-0.148	-0.183	-0.125	-0.166	-0.512	-0.492	-0.124	-0.291
N2	-0.031	0.045	-0.308	-0.043	0.113	0.120	-0.045	-0.109
N3	0.019	0.055	0.741	-0.100	-0.730	-0.369	0.162	0.081
C4	-0.246	-0.393	-0.597	-0.061	-0.007	-0.135	-0.225	-0.180
C5	0.334	0.319	0.381	0.290	0.820	0.778	0.227	0.963
H6	0.147	0.216	0.194	0.095	0.309	0.206	0.131	0.077
O7	-0.316	-0.282	-0.333	-0.298	-0.627	-0.605	-0.342	-0.872
C8	0.034	0.004	-0.225	0.104	0.359	0.253	0.027	0.217
C9	-0.026	-0.102	-0.052	-0.054	-0.215	-0.132	-0.085	-0.039
C10	-0.044	-0.127	-0.107	-0.062	-0.225	-0.167	-0.104	-0.064
C11	-0.064	-0.040	-0.022	0.031	-0.060	0.008	0.016	-0.013
C12	-0.044	-0.128	-0.109	-0.062	-0.227	-0.168	-0.102	-0.025
C13	-0.016	-0.089	-0.024	-0.047	-0.201	-0.108	-0.071	-0.028
C14	0.071	-0.189	-0.078	-0.185	-0.589	-0.347	-0.253	-0.001
H15	0.082	0.155	0.119	0.074	0.259	0.167	0.111	0.043
H16	0.072	0.147	0.123	0.085	0.278	0.192	0.121	0.058
H17	0.072	0.148	0.120	0.075	0.261	0.168	0.112	0.044
H18	0.086	0.162	0.135	0.103	0.304	0.212	0.129	0.074
H19	0.007	0.097	0.054	0.072	0.226	0.135	0.103	0.020
H20	0.005	0.091	0.058	0.076	0.227	0.136	0.104	0.021
H21	0.005	0.092	0.055	0.073	0.238	0.147	0.108	0.026

^a Distributed multipole analysis.

the nitrogen atom, N3, is negatively charged, with the 3-21G method giving the largest value and the STO-3G method the smallest, and the 6-31G** basis set giving values which are approximately mid-way between the other two. The STO-3G basis set gives a negative charge at N2, in common with the MNDO and PM3 methods, while the extended basis set calculations give a positive value. All the methods give a negative value for the ring carbon, C4. The additional basis functions present in the 6-31G** method do not materially affect the trends found in the charges obtained at the simpler 3-21G level though the magnitude at the ring nitrogen N3 is markedly reduced.

However, the Mulliken results obtained here, can be criticized because the method apportions overlap charge equally between a given set of atoms, and strictly, is only valid for homonuclear systems. The Lowdin method²⁰ in contrast, which is based on a molecular wavefunction written in terms of a basis set of orthogonalized atomic orbitals, gives a somewhat different charge distribution at the 6-31G** level (Table 3) to that obtained by the Mulliken population analysis. The main difference found here is a reversal in the sign of the charges at the N2 and N3 positions with the Lowdin method giving negative and positive values respectively, *versus* the reverse for the Mulliken method. The positive charge at N3 and negative charge at C4 obtained with the Lowdin method is similar to those calculated with the semiempirical methods and support the resonance structure **1b**.

Similar trends are obtained from a distributed multipole analysis (DMA)²¹ of the 6-31G** wavefunction (Table 3). The charge calculated at each atom centre using this procedure, shows similar trends to the Lowdin method though the magnitude of the positive and negative charges at N3 and C4 is smaller. However, the method produces a very large polarization of the carbonyl group of the sydnone ring with a formal charge of almost +/−1 at C5 and O7 and a very small polarization of the carbon and hydrogen atoms of the phenyl ring (Table 3) and is therefore unsatisfactory.

None of the calculated dipole moments match the experimental values of 6.98 D²² and 6.89 D²³ recorded in benzene. At the semiempirical level, the MNDO method gives the best result at 7.47 D, while the STO-3G basis set gives the best value for the *ab initio* methods at 7.40 D (Table 2). The

3-21G basis set gives a poor result by comparison with experiment and although the addition of more basis functions would be expected to improve greatly the result, the 6-31G** calculation shows only a marginal improvement over the 3-21G value.

Conformational Aspects.—The geometry optimization of 3-(4-tolyl)sydnone (**1b**) at the 6-31G** level gives a twisted structure with a 31° torsion angle at the phenyl ring (Table 2). However, the crystallographic data for the closely related 3-(4-ethoxyphenyl)sydnone (**1c**), which is planar, and 3-(4-isopropoxyphenyl) sydnone (**1d**), which is twisted around the N-phenyl bond, suggest that there is little difference in energy between these conformations. A further structure optimization was carried out at the 6-31G** level, therefore, to explore this aspect on 3-(4-tolyl)sydnone (**1b**) with both aromatic rings constrained to lie in the same plane.

The resulting geometry is similar to that obtained for the unconstrained optimizations with only very small differences found in the bond lengths. For example, the O1–N2, N2–N3 and N3–C4 values of 1.329, 1.263 and 1.335 Å are almost identical with those found in the twisted structure at 1.331, 1.263 and 1.335 Å, respectively (Table 2). The largest change, however, would be expected at the bond between the rings, but even here there is little difference between the planar conformer with N3–C8 = 1.439 Å *versus* a value of 1.435 Å in the twisted conformer. Overall, the planar conformer is calculated to be only 1.38 kcal mol^{−1} higher in energy than the twisted conformer and this small difference helps to explain why some of the phenylsydnones are planar and others twisted.

As far as the electronic properties are concerned, however, there are some significant differences between the planar and twisted conformers. Thus the Mulliken charges at the C8 and N3 positions in the twisted conformer, change from 0.253 and −0.369 (Table 3) to 0.284 and −0.401, respectively, in the planar conformer reflecting the increased overlap at these atomic centres. The effect is much smaller at the adjacent atoms N2 and C4 of the sydnone ring which change from 0.120 and −0.135 in the former to 0.124 and −0.125 in the latter. As a result of the changes in charge distribution, the dipole moment of the twisted conformer increases from 9.209 to 9.213 D in the planar structure.

Conclusions

Neither the semiempirical MNDO, AM1 and PM3 methods nor the *ab initio* STO-3G, 3-21G and 6-31G** basis sets give a satisfactory account of the structure of 3-(4-tolyl)sydnone by comparison with the well resolved crystal structure. Surprisingly, the 6-31G** basis set shows little if any advantage over the simpler 3-21G approach. The calculated charge distributions of atoms in the heterocyclic ring vary with the theoretical method adopted and also in the case of the *ab initio* basis sets, the method of wavefunction analysis. The calculated dipole moments are generally unsatisfactory with the best results obtained with the MNDO method for the semiempirical procedures and the STO-3G basis set for the *ab initio* methods.

It is clear from these results that more extensive calculations are required to reproduce the experimental geometry on the one hand and the electronic properties (in terms of the dipole moment) on the other using perhaps a multi-configuration interaction treatment of the valence electrons. Furthermore, because the calculated geometries described here relate to the isolated molecule only, it may be necessary to include a representation of the electrostatic field (perhaps in terms of a series of point charges) in order to correlate the calculated results with those found experimentally in the crystal environment. Such an approach, however, for the relatively large 3-(4-tolyl)sydnone molecule requires considerably more computing resources than those that were available for this study.

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