

The Polar Nature of 2,1,3-Benzoxadiazole, -Benzothiadiazole, -Benzoselenadiazole and Derivatives as Determined by Their Electric Dipole Moments

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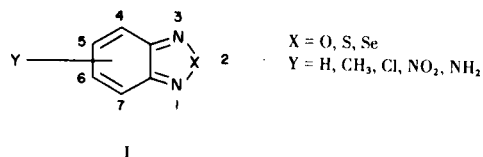
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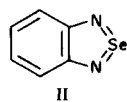
Permanent electric dipole moments have been determined in benzene solutions at 25° for the oxygen, sulfur, and selenium series of 2,1,3-benzodiazoles. The derivatives studied contained 4, 5, and 6 substituted methyl, chloro, nitro, and amino groups. The dipole moment data of the derivatives were analyzed relative to that of the parent species which allowed deductions to be made about the mesomeric structures operating in the compounds. The mesomeric charge transfer increases regularly from the oxygen to the selenium structures, being nearly undetected in 2,1,3-benzoxadiazole derivatives and very pronounced in the 2,1,3-benzoselenadiazoles.

Introduction.

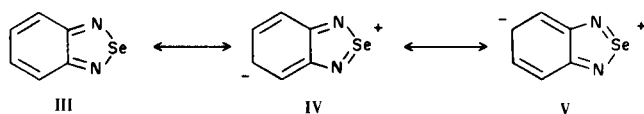
This paper reports on the systematic investigation into the polar nature of the 2,1,3-benzodiazole system, through measurement of their electric dipole moments.



Aromatic heterocyclic compounds containing the group VI elements, oxygen, sulfur, and selenium offer an excellent series to investigate the influence of the heteroatom on molecular electronic properties. Considerable interest has been shown in the nature of the polarity, bond fixation and the d-orbital influence in the compounds containing sulfur and selenium. The results of an early dipole moment study (1) indicated that contributions of forms like



are important to the overall structure of 2,1,3-benzoselenadiazole and the structures of sulfur analogues probably are similar. In addition other mesomeric forms that might be important are:



This would hold for both sulfur and selenium conjugated systems. However, X-ray crystal structure work by Luzzati (2) indicated that the N-O and N-S had double bond lengths whereas the N-Se bond length showed considerably more single bond character. X-ray structure data, single bond and double bond comparison as well as comparable data for the analogous 1,2,5 diazoles is shown in Table I. In addition the C₄-C₅ bond lengths were found to be 1.30Å and 1.29Å for 2,1,3-benzoselenadiazole and 2,1,3-benzothiadiazole, respectively, but 1.43Å for 2,1,3-benzoxadiazole. The above data appears to be in contradiction to the proposed structures from the dipole moment study (1), which indicated that the Se compound might have the greatest aromatic character. Linnett and Rosenberg (3) have applied the Linnett model to explain these crystal structures, especially the apparent abnormality in the NO bond length found in 2,1,3-benzoxadiazole. This they did by proposing a resonance form primarily within the five membered ring. They also concluded in their interpretive study that the S and Se compounds must be retaining much of the classical fixed bond structure. By contrast, the proton magnetic resonance work on these compounds (4,5) supported fixed bonds in the six membered ring for 2,1,3-benzoxadiazole and more aromatic character for the S and Se compounds. Electron paramagnetic resonance studies (6,7) have examined the electron charge distribution and found little effect in their calculations by including d-orbitals which structure II would imply. Additional studies include a structural uv study (8) and synthesis (9).

This investigation examines the structural problem

TABLE I
Comparison of Bond Lengths (Å) Between 2,1,3-Benzodiazoles, 1,2,5-Diazoles and Those Expected for Single and Double Bonds

	N-Se	C=N	N-S	C=N	N-O	C=N
2,1,3-Benzodiazoles (a)	1.83	1.30	1.60	1.34	1.20	1.35
1,2,5-Diazoles	1.830 (c)	1.30 (c)	1.631 (d)	1.328 (d)	1.38 (e)	1.30 (e)
Standard single bonds (b)	1.87		1.67- 1.74		1.30- 1.40	1.42- 1.47
Standard double bonds (b)	1.67		1.60		1.06- 1.22	1.34

(a) Reference 2, X-ray data. (b) *Tables of Interatomic Distances, Chem. Soc. London, (1958)*. (c) Reference 33. (d) Reference 32. (e) Reference 34.

through a dipole moment study on a complete series of selected 2,1,3-benzodiazole derivatives. Comparing experimental dipole moments in a systematic way to those calculated for the compounds using the parent compound value as a group moment gives insight as to what mesomeric structures are operative and important.

EXPERIMENTAL

Dipole Moments.

The dielectric constants were measured at $25 \pm 0.02^\circ$ using a Wiss.-Techn. Werkstätten D812 Weilheim Dipolometer DMO1 with the DFL-2 Cell. The refractive indices were measured at $25 \pm 0.02^\circ$ using a Bausch and Lomb Precision Refractometer. Baker Analyzed benzene was refluxed and distilled from calcium hydride and further dried over Baker Analyzed or Linde type 4A molecular sieve. Baker Analyzed dioxane was prepared for use by refluxing over sodium and distilling onto molecular sieve which had been previously activated at 350° . The refractive indices found for benzene and *p*-dioxane at 25° were 1.49796 and 1.42002, respectively. The dipole moments were evaluated by the method of Guggenheim (10) with all the data treated by least squares. Solutions used for dielectric constant measurement ranged from 0.5 to 4 weight per cent. Standard deviations were derived from the least squares data and applied by the method of maximum probable error to the final dipole moments using 95 percent confidence limits. All calculations were performed using a complete dipole moment program and error analysis routine written for our Control Data 3100 Computer.

Material Preparation.

With the exception of those noted below, the benzodiazoles used in this study were obtained commercially. Pertinent data on melting points and analysis of the compounds studied is listed in Table II. All samples were purified either by sublimation or by recrystallization from ethanol.

2,1,3-Benzoxadiazoles (i-iii).

The appropriate *o*-nitroaniline was oxidized with sodium hypochlorite to the corresponding 2,1,3-benzoxadiazole *N*-oxide (benzofuroxan) by the procedure of Green and Rowe (22). The *N*-oxide was then reduced with hydroxylamine to give the 2,1,3-benzoxadiazole by the method of Zincke and Schwarz (23).

A recent description of these two procedures is given by Gaughran, Picard, and Kaufman (12).

The 2-nitro-4-methyl-5-chloroaniline needed for the preparation of 5-methyl-6-chloro-2,1,3-benzoxadiazole (III) was obtained from 3-chloro-4-methylaniline as yellow crystals, m.p. $163-164^\circ$ (lit. m.p. 165°) (24), in an overall 60% yield by using the general procedure of Porter and Peterson (25).

2,1,3-Benzothiadiazoles (vi, viii-x).

The appropriate *o*-nitroaniline in *N,N*-dimethylformamide was catalytically reduced to the corresponding diamine by a procedure similar to that described by Adams and Cohen (26). Because the diamines oxidize very rapidly when exposed to air, they were usually not isolated but rather the *N,N*-dimethylformamide solution of the diamine was used directly in the next step which involved conversion to the thiadiazole by reaction with sulfur monochloride as described by Weinstock *et al.* (27).

5-Nitro-2,1,3-benzothiadiazole (ix) was prepared in the same manner by reacting sulfur monochloride with the commercially available 4-nitro-*o*-phenylenediamine.

2,1,3-Benzoselenadiazoles (xii, xiv, xv).

These derivatives were synthesized from the appropriate diamines by reaction with selenium dioxide using a procedure which is similar to the method described by Sawichi and Carr (20).

Results and Discussion.

Table III lists the dipole moments for the compounds studied, and their probable statistical errors. Values for the compounds that have been run before by Hill and Sutton were in good agreement with ours except for 2,1,3-benzoselenadiazole, which was nearly 0.26 Debyes smaller. We redetermined the dipole moments for the parent compounds so a self-consistent set of data could be obtained for calculation and comparison purposes. All of the values were obtained in benzene except for 5-nitro-2,1,3-benzoselenadiazole which was run in *p*-dioxane. A possible solvent effect was checked by determining the dipole moment of 5-nitro-2,1,3-benzothiadiazole in *p*-dioxane. The value of 2.70D agreed closely with that listed for this compound in benzene. Since the dipole

TABLE II
 Characterization Data for 2,1,3-Benzodiazole Series

Compound	R ₁	R ₂	R ₃	X	M.p. (corrected), °C	M.p. (Lit.), °C	Formula	% C		% H	
								Calcd.	Found	Calcd.	Found
i	H	H	H	O	51.4-52.3	55 (11)					
ii	H	CH ₃	H	O	34.7-35.6	37 (12)					
iii	H	CH ₃	Cl	O	51.8-52.6		C ₇ H ₅ ClN ₂ O	49.87	49.93	2.99	3.07
iv	H	H	H	S	42.8-44.0	44 (13)					
v	NH ₂	H	H	S	65.1-66.3	68 (14)					
vi	CH ₃	H	H	S	b.p. 77.5-79.5 (b) (2.5 torr.) n _D ^{25.0} 1.6259	b.p. 229.5- 230.5 (15) n _D ²⁰ 1.6265	C ₇ H ₆ N ₂ S	55.98	55.87	4.03	4.11
vii	NO ₂	H	H	S	107.0-107.9	109 (16)					
viii	H	CH ₃	H	S	29.6-30.5	34 (17)					
ix	H	NO ₂	H	S	127.6-128.6	128 (17)					
x	H	CH ₃	Cl	S	81.7-82.4		C ₇ H ₅ ClN ₂ S	45.53	45.75	2.73	2.68
xi	H	H	H	Se	73.1-74.2	76 (13)					
xii	CH ₃	H	H	Se	110.4-111.0	110.6-111.2 (18)	C ₇ H ₆ N ₂ Se	42.66	42.59	3.07	3.14
xiii	H	CH ₃	H	Se	69.2-70.4	73 (19)					
xiv	H	NO ₂	H	Se	222.4-223.7	224 (20)					
xv	H	CH ₃	Cl	Se	147.3-148.2		C ₇ H ₅ ClN ₂ Se	36.31	35.98	2.18	2.16
xvi	H	CH ₃	CH ₃	Se	143.5-144.5	144 (21)					

(a) Galbraith Laboratories, Knoxville, Tennessee. (b) Uncorrected.

TABLE III
Experimental Dipole Moments for the
2,1,3-Benzodiazole Series at 25° in Benzene

Substitution	O	S	Se
None (a)	4.04 ± 0.03	1.79 ± 0.03	1.19 ± 0.03
5-Methyl	4.45 ± 0.02	2.22 ± 0.03	1.84 ± 0.06
5-Chloro (b)	2.88	0.84	0.50
5-Chloro-6-methyl	3.38 ± 0.02	1.32 ± 0.03	1.04 ± 0.05
4-Methyl		1.84 ± 0.02	1.20 ± 0.04
5,6-Dimethyl			2.13 ± 0.03
4-Nitro		4.08 ± 0.02	
4-Amino		2.46 ± 0.23	
5-Nitro		2.75 ± 0.02	3.59 ± 0.02 (c)

(a) All values agree with those determined by Sutton except 2,1,3-Benzoselenadiazole which is 0.26 Debyes higher in this work.
(b) Reference 1. (c) Value determined in *p*-dioxane.

moment increased with the addition of methyl groups to the ring and decreased when a chlorine was substituted onto the ring, the dipole moment for the parent compounds was taken to be down the C_{2v} symmetry axis, with its negative end pointing toward the O, S, or Se heteroatom.

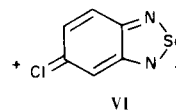
One method to use in examining the structural effects through dipole moment data is to calculate the dipole moment of the parent compound using reasonable bond moments determined from similar structures. Comparison of calculated and observed dipole moments can show unusual behavior. Hill and Sutton applied this method to the parent compounds using approximate geometries. We have done similar calculations using the X-ray data (2), taking the CN bond moment as 1.4D, and calculating the NX bond moment from the following equation (28),

$$\mu_{NX} = 4.8 r_{NX} [1 - e^{-0.25(\Delta\chi)^2}]$$

In this equation r_{NX} is the bond length between the nitrogen and heteroatom, and $\Delta\chi$ is the difference in electronegativity between the two atoms. Our calculated values are 3.1 D, 2.0 D, and 2.0 D for 2,1,3-benzodiazole, 2,1,3-benzothiadiazole and 2,1,3-benzoselenadiazole, respectively. Hill and Sutton's corresponding values for these compounds are 2.86 D, 1.76 D, and 1.64 D. The conclusions drawn from our calculated results to explain their difference from the experimental values would be similar to that of Hill and Sutton. However, to better understand the electric effects which determine the dipole moment we choose to base our detailed analysis on the experimental parent dipole moments and reliable substituent group moments.

To use this series of compounds in such a systematic analysis, the parent compounds' dipoles were assigned for the group moment of that structure in all of the derivatives. The methyl group, chlorine atom, and nitro groups were assigned values of 0.43 D, 1.58 D, and 3.93 D respectively, from toluene, chlorobenzene and nitrobenzene (29). Then taking the benzene ring angles to be unperturbed, the vector addition for ring substitution is easily carried out.

The results showing the calculated dipole moments, observed dipole moments and their differences are found in Table IV, and the dipole moment angle with respect to the symmetry axis of the parent is also given. The negative angle is measured from the heteroatom in a clock-wise direction. The purpose in putting the data in this form is to allow observation of a difference between the three structures. In examining this table, note that the parent molecule is used for a group moment which contains much of the initial mesomeric information. However, the substitution of various groups should increase or decrease the stability of various contributing polar structures, and therefore, should show apparent differences between experimental and calculated dipole moments. Examination of these differences in Table IV shows some interesting trends. In placing a chloro group at position 5 or 6, it might be predicted that the mesomeric contribution of the type illustrated by form IV or V, would be reduced, causing the experimental dipole moment to be lower than calculated. That is, a charged mesomeric structure like that shown by VI gives rise to a mesomeric moment which is in opposition to the main dipole.



The small effect, positive $\Delta\mu$, in the 2,1,3-benzodiazole which increases ($\Delta\mu$ large and negative) in going to 2,1,3-benzoselenadiazole would indicate that the mesomeric contribution of type IV and V are most important for the Se compound. Throughout Table IV the standard errors are smaller than the differences in the trends shown for $\Delta\mu$.

The electropositive methyl group would also tend to decrease the mesomeric stability of form IV or V which would result in the observed dipole moment becoming larger relative to the parent structure. This effect should be greatest for the parent species having the largest original mesomeric contribution. Note the consistent increase in going from the O to the Se compounds. This effect is verified in 5,6-dimethyl-2,1,3-benzoselenadiazole.

It would appear, then, that in the 5-chloro-6-methyl series there should be a combined effect, with the chlorine

TABLE IV
Observed and Calculated Electric Dipole Moments (a)

Compound	$\mu_{\text{Obs.}}$	$\mu_{\text{Calc.}}$	$\Delta\mu$	$\theta_{\text{Calc. deg.}}$
5-Chloro				
O	2.88	2.79	0.09	16.4
S	0.84	0.90	-0.06	61.4
Se	0.50	0.81	-0.31	102.8
5-Methyl				
O	4.45	4.42	0.03	-2.8
S	2.22	2.17	0.05	-5.7
Se	1.84	1.58	0.26	-7.8
5,6-Dimethyl				
Se	2.13	1.94	0.19	0
5-Chloro-6-Methyl				
O	3.38	3.21	0.17	18.2
S	1.32	1.28	0.04	51.7
Se	1.04	1.02	0.02	80.2
5-Nitro				
S	2.75	2.54	0.21	129.3
Se	3.59	2.96	0.63	138.4
4-Amino				
S	2.46	2.35	0.11	-40.5
4-Nitro				
S	4.04	4.32	-0.28	65.5
4-Methyl				
S	1.84	1.84	0	-13.5
Se	1.20	1.26	-0.06	-20.0

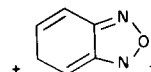
(a) In Debye units.

effect being dominant. The group dipoles, remember, work in opposite directions. The smaller downward trend in moving from the oxygen to the selenium heteroatom does bear this out.

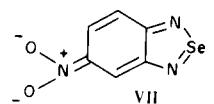
Finally, it would be expected that nitro group substitution on position 5 or 6 to have the largest effect with the selenium compound. This was found to be true. Nitro group substitution effects on 2,1,3-benzoxadiazole would be expected to be minimal. The results bear this out. At first glance it would seem that $\Delta\mu$ should be negative rather than positive for nitro substitution, like for chlorine. However, this vector addition must not only be examined by magnitudes, but also by direction. In this case, the mesomeric moment and substituent group moment (and induced moment) would tend to be in the same direction, and the observed dipole would then be larger than calculated. The $\Delta\mu$ should be a larger positive value for a structure with a larger mesomeric contribution at that position.

The data in this study seems consistent with a decreasing mesomeric character for the compounds $\text{Se} > \text{S} > \text{O}$. The 2,1,3-benzoxadiazole mesomeric effect into the six membered ring appears to be small. The order of decreasing aromatic character would follow the same pattern. Consequently, since the C-N bonds are not localized in 2,1,3-benzoxadiazole according to X-ray crystal structure data, and the dipole moment is calculated to be lower than what is observed, then the primary mesomeric contribution to this structure must be within the five membered ring. This is consistent along with Rosenberg's explanation (3), and fits interpretations given for 1,2,5-oxadiazole derivatives (30). Furthermore, if this effect is not transferred into the non heterocyclic aromatic ring, it also accounts for the fixed orthoquinone structure as indicated by the larger J_{45} and smaller J_{67} coupling constants found by nmr (4,5). This also would account for the fact that in the 5-chloro-6-methyl-2,1,3-benzodiazole series, only the oxygen compound shows a distinct coupling to the methyl group of nearly 1 Hz (31).

On occasion where substitution of chlorine at position five gave a small positive $\Delta\mu$ for 2,1,3-benzoxadiazole, it could be accounted for by a slight contribution from a structure like



Proceeding through any series to the selenium compounds, one observes the largest $\Delta\mu$ values. This indicates that 2,1,3-benzoselenadiazole is very much prone to this 5,6 mesomeric transfer as shown in structure IV and V. The largest effect is found with the 5-nitro substitution, due probably to the following structure:



This structure must account for the unusually high melting point compared to 5-nitro-2,1,3-benzothiadiazole, and the large increase of the observed dipole moment over that calculated. A similar conclusion was made for this structure from a uv study (20). This increased aromatic character predicted for the six membered ring in the S and Se compound also correlates with the nmr studies (5,6).

One interesting comparison, see Table I, is to examine the differences between the 1,2,5-diazoles and the 2,1,3-benzodiazoles. In the S and Se compounds, the similarities are apparent, but the differences in the O compound are striking. The N-O bond length in 1,2,5-oxadiazole is much more like a single bond. The X-ray data do not appear to be consistent with this. Interestingly, the

dipole moments of 1.56 and 1.11 for 1,2,5-thiadiazole (32) and 1,2,5-selenadiazole (33) are similar to the analogous 2,1,3-benzodiazoles, but the value of 3.38 D for 1,2,5-oxadiazole (34) is significantly less, in fact, comparable to the calculated one.

In conclusion, making this type of self-consistent dipole moment comparison for a systematic series of compounds allows one to make deductions of electronic changes in the parent compound without being plagued with many of the difficulties of computing dipole moments from independently derived bond moments. From this study, it seems apparent that the 2,1,3-benzoxadiazole compound primarily is in the orthoquinone structure with resonance primarily occurring with the five membered ring. The main structures put forth by Hill and Sutton to explain that large dipole moments do not seem warranted. The S and Se analogues show increasing aromatic character respectively, with the greatest amount of mesomeric contribution occurring in the selenium compound. The classical structures for the S and Se parent species discussed by Linnett and Rosenberg (3) are not consistent with this data. Since these present dipole moment results appear consistent with a number of independent studies, but not the X-ray structure data, it would appear that the structure data for this series needs to be reinvestigated.

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