Tetrahedron. Vol. 27, pp. 767 to 774. Pergamon Press 1971. Printed in Great Britain

THE CONFORMATION OF THIETANE DERIVATIVES

S. KUMAKURA, T. SHIMOZAWA
Department of Chemistry, Saitama University, 255 Shimo Okubo, Urawa-shi, Saitama, Japan

Y. OHNISHI and A. OHNO
Sagami Chemical Research Center, Ohnuma, Sagamihara-shi, Kanagawa, 229, Japan

(*Received in Japan* 8 *August* 1970; *Received in the UK for publication* 18 *August* 1970)

Abstract—The dipole moments of thietane derivatives were measured by the solution method, using benzene as a solvent; by comparing the observed and calculated values of these dipole moments the conformations and bond moments were also determined. 2,2-Diphenyl-3,4-dicyanothietane and 2,2-diphenyl-3,4-dichlorothietane have the same configuration as that of the corresponding ethylene derivatives, the starting materials in the synthesis of these compounds. The C—Cl bond moments, found in 2,2-diphenyl-3,4-dichlorothietane, have different values, 1·40 D and 2·10 D. These values are significantly different from the usual values. Seemingly the lone pairs located on the S atom make an important contribution to the increment of the bond moment at C_4 and the decrement at C_3.

The puckering motion of the thietane skeleton of these compounds was not observed in the temperature range of 25–40°, i.e. no significant variation in the dipole moments in the range could be detected.

INTRODUCTION

THE mechanism of the photocycloaddition of thiobenzophenone to olefines activated by electron-withdrawing groups, which produce thietane derivatives, has been investigated. It has been reported that the reactions should involve nucleophilic attack by the π, π^* singlet state of thiobenzophenone or a charge transfer from the π, π^* state of thiobenzophenone to the electron-deficient double bond.[1] In order to support this postulation, it was necessary to determine the configurations of the reaction products and to compare them with those of the corresponding ethylene derivatives used as reactants.

Usual spectroscopic methods failed to determine the configurations of the reaction products, but the dipole moment study was expected to be favorable for the purpose, because the molecules have strongly polar groups.

The dipole moment of thietane was obtained by Comper *et al.*,[2] but those of thietane derivatives have not been measured. Hence these measurements were undertaken to establish the molecular conformations and to investigate the bond nature of the C—Cl bonds. The dipole moments of dioxy- and oxy-diphenylthietane derivatives were also measured to investigate the interesting feature of the nonbonded Cl···S interaction.

EXPERIMENTAL

Synthesis and purification of materials. Thietane I (b.p. 75°) was obtained by fractional distillation of a commercial material. Compounds II, III, IV or V were synthesized by a photochemical reaction using UV irradiation ($\lambda = 3660$ Å). Compounds VI or VII and VIII were prepared from compounds IV and V by oxidation using 30% H_2O_2.[1] These materials were purified by column chromatography and recrystallization. The structures were identified by mass, IR, and NMR spectroscopy as well as elementary analyses.

Measurement of dipole moments. The dipole moments were obtained by measuring dielectric constants and densities of dilute solns as functions of the concentration at 25·0°. Dielectric constants (ε) were measured by the usual hetrodyne-beat method.[3] The experimental errors in measured ε were within

$\pm 0{\cdot}0002$. All the measurements were performed in benzene as solvent. Densities were measured by an Ostwald picnometer. Dipole monents were calculated[*] by Halverstadt–Kumler's equation.[4]

Molecular refraction (MR_D) was measured for thietane by observing the refractive index of dilute solutions of the compound. It was found that the value of MR_D is smaller than the value calculated by the additivity of atomic re-fractions by 1·16cc, which might be caused by the atomic refraction of the 4-membered ring.

Thus, the electronic polarizations (P_E) for the series of the compounds were calculated by adding the

TABLE 1. DIELECTRIC CONSTANTS AND DENSITIES OF BENZENE SOLUTIONS AS A FUNCTION OF THE CONCENTRATION (25·0°)

Compounds	Concentration (wt%)	Dielectric constants	Density g/cm^3
I	0·00	2·2724	0·8737
	1·02	2·3180	
	1·39	2·3348	0·8751
	2·86	2·4011	0·8769
	2·88	2·4033	
	4·97	2·5036	
	5·72	2·5364	0·8801
II	0·00		
	1·51	2·3726	0·8778
	4·00	2·5307	0·8851
III	0·00		
	1·94	2·3268	0·8784
	4·85	2·4094	0·8850
IV	0·00		
	0·88	2·2889	
	0·90	2·2910	0·8771
	2·11	2·3172	0·8805
	2·59	2·3256	
	4·44	2·3693	0·8872
V	0·00		
	0·94	2·2894	0·8771
	1·07	2·2931	
	2·21	2·3125	0·8807
	2·26	2·3125	
	3·86	2·3434	0·8857
VI	0·00		
	1·12	2·3506	0·8779
	2·58	2·3732	0·8808
VII	0·00		
	1·24	2·3202	0·8770
	2·58	2·3732	0·8820
VIII	0·00		
	0·61	2·2970	0·8758
	1·34	2·3280	0·8780

---

[*] Calculations were carried out on the *TOSBAC* 3400 Computer at this University.

TABLE 2. POLARIZATIONS AND DIPOLE MOMENTS OF THIETANE AND ITS DERIVATIVES (25·0°)

Compounds	P_2 (cc)	$P_E + P_A$ (cc)	P_0 (cc)	μ(obs) (D)
I	81·49	21·51	59·98	1·72
II	400·64	99·25	301·39	3·83
III	196·84	85·69	111·15	2·32
IV	178·35	82·36	95·99	2·16
V	165·81	82·36	83·45	2·02
VI	504·39	87·11	417·28	4·51
VII	311·54	87·11	224·43	3·32
VIII	306·26	84·68	221·58	3·29

atomic refractions of all the atoms in each compound and the value of −1·16cc for the 4-membered ring. The atomic polarization (P_A) was assumed to be 5% of P_E for all compounds.

Dielectric constants, densities, and dipole moments (μ) measured at 25·0° are listed in Tables 1 and 2. The experimental errors in the dipole moments were within ±0·02 D.

DISCUSSION

The Skeletal Configuration and the Dipole Moment of Thietane

For the purpose of calculating the dipole moments of thietane derivatives, the following assumption was made: the skeletal dimensions of thietane are the same as those in the skeleton of the phenyl substituted thietane. The precise molecular geometry of thietane had been determined by microwave study[5] and is shown in Fig 1. Because the

TABLE 3. COMPARISON BETWEEN OBSERVED AND CALCULATED DIPOLE MOMENTS, CORRESPONDING TO POSSIBLE CONFORMATIONS, OBTAINED BY ASSUMED BOND MOMENTS: $\mu_l(CCl) = 1·6(D)$, $\mu_l(CC\equiv N) = 3·6(D)$, $\mu(CC\equiv N) = 4·0(D)$, $\mu_g(S{=}O) = 2·8(D)$, AND $\mu(S{=}O) = 2·0(D)$

Compounds	Positions and directions of substituents	μ(calc) (D)	μ(obs) (D)
I	—	—	1·72
II	3*a*4*a*	0·72	3·83
	3*e*4*e*	3·80	
III	3*a*	4·49	2·32
	3*e*	2·38	
	4*a*	3·68	
	4*e*	4·42	
IV	3*a*4*e*	3·21	2·16
	3*e*4*a*	1·94	
V	3*a*4*a*	1·24	2·02
	3*e*4*e*	1·55	
VI	3*a*4*e*	5·35	4·51
	3*e*4*a*	2·99	
VII	3*a*4*a*	4·00	3·32
	3*e*4*e*	3·40	
VIII	1*a*3*a*4*e*	5·97	3·29
	1*a*3*e*4*a*	1·23	
	1*e*3*a*4*e*	3·74	
	1*e*3*e*4*a*	4·44	

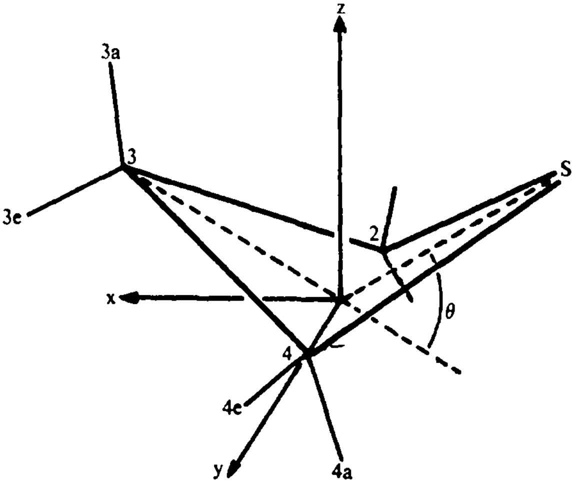


FIG 1. Skeletal configuration and dimensions of thietane
Bond lengths and angles: C—S = 1·819 A; C—C = 1·549 A;
HCH = 110° 18′; $C_2C_3C_4$ = 84°33′; Dihedral angle (θ) = 40°

bond moment of the phenyl substituents was presumed to be zero, it was assumed that the observed moment of thietane, obtained by the authors, could be used as a skeletal moment of all the phenyl substituted compounds, even though the value was 0·06 D smaller than that obtained by Cumper *et al.* As a first approximation, dipole moments of all compounds, corresponding to all conceivable conformations, were calculated by assuming the usual bond moments[6] and the dihedral angle of 40°, as is found in thietane. The calculated values of dipole moments are listed in Table 3, together with the observed values.

Determination of conformations

Diphenylthietane derivatives

trans-2,2-*Diphenyl*-3,4-*dicyanothietane* (II) *and* 2,2-*diphenyl*-3-*cyanothietane* (III). Stereochemically it could be expected that II would have one of the two possible conformations denoted by 3*e*4*e* and 3*a*4*a*, in which 3*e* and 3*a* mean an equatorial and an axial direction of the substituent group at the position C_3, and that the direction of the substituent in III would be either 3*e* or 3*a*. Dipole moments calculated for II and III were obtained by assuming the following bond moments; μ_i (CC≡N) = 3·6 D and μ (CC≡N) = 4·0 D, where the suffix *i* means a substituent at a *vic* position in a disubstituted compound. The calculated values are listed in Table 3. In this Table, the values calculated for 3*e*4*e* of II and 3*e* of III agree well with the observed values.

The calculated values were re-examined changing the dihedral angle in steps over the range of 0–90° in order to obtain the dependence of the dipole moments on the dihedral angle (θ). These are shown in Figs. 2a and 2b as a function of the angle (θ), where the angle is dotted on the abscissa and the μ_{calc} on the ordinate. These figures show that an assumption of 40° for the dihedral angle is the unique value leading to good agreement, and that the deviation of μ_{calc} in $\Delta\theta = \pm 5{\cdot}0°$ is less than 0·10 D. Therefore, the difference in the dihedral angle between those of the two compounds and of thietane would be negligibly small.

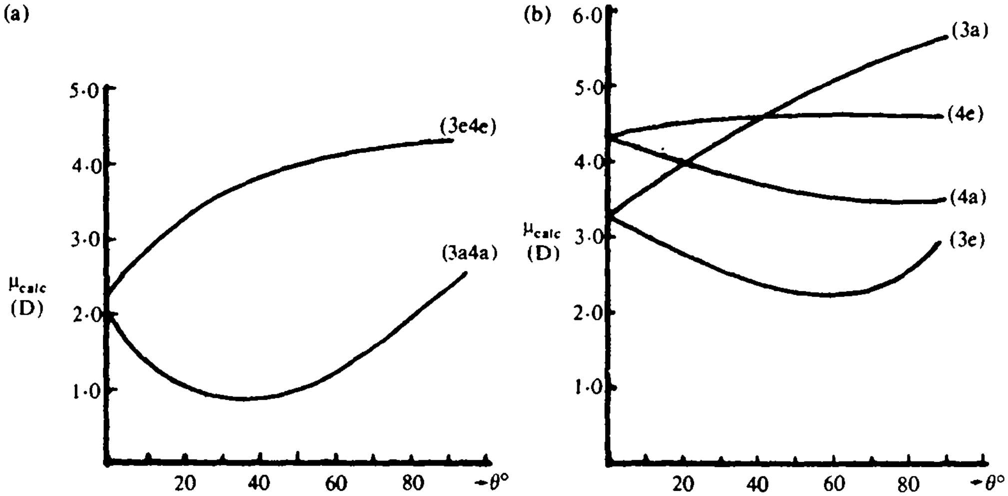


FIG 2. Dependence of calculated dipole moments of thietane derivatives on the dihedral angle
(a) Compound II; (b) Compound III

The μ_{calc} of II was also checked by changing the $CC{\equiv}N$ bond moments over a possible range 3·0–5·0 D at a fixed dihedral angle of 40°. It was found that the assumed bond moments were reasonable.

The results obtained can be summarized as follows: Compound II has the conformation 3*e*4*e* with $\theta = 40°$ and $\mu\ (CC{\equiv}N) = 3{\cdot}6$ D at both positions C_3 and C_4. Compound III has the conformation 3*e* with $\theta = 40°$ and $\mu\ (CC{\equiv}N) = 4{\cdot}0$ D at position C_4.

It is noteworthy that all the $CC{=}N$ bond moments in II and III are normal.

cis- *and* trans-2,2-*Diphenyl*-3,4-*dichlorothietane* (IV and V). The calculated dipole moments of IV and V for all of their possible conformations were obtained by assuming the CCl bond moment to be 1·6 D; and these are listed in Table 3.

In this Table, agreement between the calculated and the observed values for the compounds is poor, whereas that for IV (3*e*4*a*) is fairly good. The difference between μ_{calc} and μ_{obs} was thought to be caused mainly by the following two factors: (1) the assumed dihedral angle was inadequate; and (2) the bond moment was not precisely assumed. First of all, the dihedral angle dependence of the calculated dipole moments was checked by changing the angle over a range of 0–90°. The results obtained suggested that the deviation in the calculated values of $\Delta\theta = \pm 5{\cdot}0°$ is less than 0·07 D, whereas for conformation V (3*e*4*e*) the value leading to good agreement is only at $\theta = 90°$, which is not allowed stereochemically. Owing to these results and also to the fact that stereochemically the distortion of the dihedral angle by replacing the cyano groups in the diphenylthietane skeleton with Cl atoms would not be more than 5°, it was assumed that the dihedral angle of both compounds is 40°, the same as found in the cyano compounds. With the dihedral angle of the compounds being thus fixed, the lack of agreement between μ_{calc} and μ_{obs} can be regarded as being due only to the bad assumption of bond moments. In order to refine the bond moments, the calculated dipole moments of the compounds were re-examined varying them over the possible range of bond moment, μ (CCl) = 1·0–2·5 D. A number of sets of μ (CCl) leading to good agreement were obtained for the conformations IV (3*e*4*a*) and V (3*e*4*e*), but not for IV (3*a*4*e*) nor V (3*a*4*a*). The sets are represented in Fig 3, where they are plotted against μ (CCl) of position C_3 indicated on the abscissa and that of position C_4 on the ordinate.

In order to choose reliable values for the CCl bond moments, it can be assumed that these bonds, corresponding to the same position in both compounds, might have common values of bond moments. The crossing point of the two curves in Fig 3, corresponding to the two conformations, was thought to be a unique set for the bond moments. Thus the following values were obtained: μ (CCl) = 2·1 D at C_4 and μ (CCl) = 1·4 D at C_3.

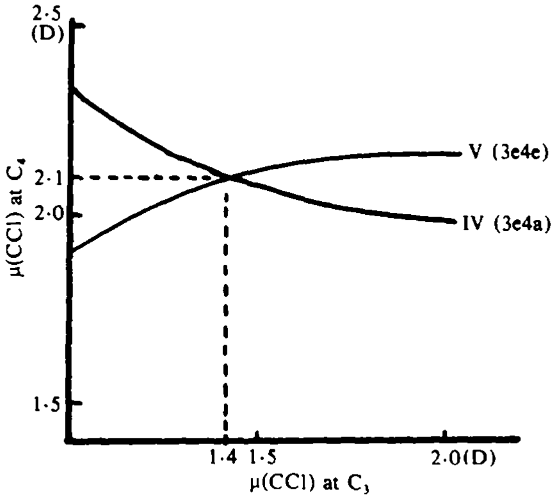


FIG 3. Optimum sets of the C—Cl bond moments of compounds IV and V

It is of interest that the difference between the bond moments at both positions C_3 and C_4 is significantly large while that of the cyano-compound was negligible. Possible explanation for the difference will be presented later.

From the results obtained for II, IV and V, it can be concluded that these compounds maintain the configurations of the corresponding ethylene derivatives, used as reactants in the photocycloaddition to produce these thietane derivatives.

1,1-*Dioxy-diphenylthietane derivatives*

cis- *and* trans-1,1-*Dioxy*-2,2-*diphenyl*-3,4-*dichlorothietane* (VI *and* VII). The calculated dipole moments of the compounds are listed in Table 3, where the following assumptions were made: μ_g (S=O) = 2·8 D, <O=S=O = 123°, and μ_t (CCl) = 1·6 D, the suffix *g* denoting the substituent at a *gem* position in the di-substituted compounds. In Table 3, the dipole moments calculated for both conformations of VI do not show good agreement with the observed value, while the calculated value for the form 3*e*4*e* of VII coincides well with the observed value. Since the valence state of sulfur is different from that of II to V, it can be expected that the dihedral angle might change. Thus in VI and VII none of the parameters could be established. In order to obtain good agreement between the calculated and the observed values, a refinement was carried out

in the dihedral angle and assumed bond moments in the following way: the observed dipole moments were compared with the calculated values obtained by varying the μ (CCl) and μ (S=O) over the possible range of values at each value of the dihedral angle over the range 0–90°. The ranges of bond moment μ (CCl) and μ (S=O) were taken as 1·0–2·5 D and 1·5–4·0 D, respectively. A reliable set of these values was obtained based on the following assumptions: (1) the bond moments at the corresponding positions in both compounds would be the same, and (2) the dihedral angles would also be the same.

The results thus obtained are as follows: (1) μ (S=O) = 2·8 D and μ (CCl) = 1·6 D at both positions C_3 and C_4, and $\theta = 15°$; (2) the conformations are VI (3*e*4*a*) and VII (3*e*4*e*).

1-*Oxy*-2,2-*diphenylthietane derivatives*

cis- 1-*Oxy*-2,2-*diphenyl*-3,4-*dichlorothietane* (VIII). By assuming that μ (CCl) is 1·6 D and μ (S=O) = 3·0 D, the dipole moments of the compound in the four possible conformations were calculated, and are listed in Table 3.

Since the conformation leading to good agreement between the observed and the calculated values could not be found in Table 3, the calculated values were re-examined changing the bond moments and the dihedral angle in the same way as described in the case of 1,1-dioxy-compounds. The possible range of variation of these parameters was taken as follows: $\theta = 0$–90°, μ (S=O) = 1·5–4·0 D, and μ (CCl) = 1·0–2·5 D. The parameters and the conformation, thus found, were as follows: μ (S=O) = 3·0 D, μ (CCl) = 1·8 D at C_4, and μ (CCl) = 1·5 D at C_3, and 1*e*3*a*4*e* with $\theta = 30°$. It is of interest to note that the results of these parameters thus obtained lie between those of VI and IV.

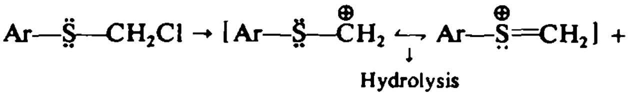
The results of all compounds are summarized in Table 4.

TABLE 4. CONFORMATIONS AND BOND MOMENTS OF THIETANE DERIVATIVES

Compounds	μ(obs) (D)	μ(calc) (D)	Conformations Arrangements	Conformations θ°	μ(CCl) at C_3	μ(CCl) at C_4	μ(CC≡N) at C_3	μ(CC≡N) at C_4	μ(S=O)
II	3·83	3·80	3*e*4*e*	40	—	—	3·6	3·6	—
III	2·32	2·38	3*e*	40	—	—	4·0	—	—
IV	2·16	2·16	3*e*4*a*	40	1·4	2·1	—	—	—
V	2·02	2·02	3*e*4*e*	40	1·4	2·1	—	—	—
VI	4·51	4·54	3*e*4*a*	15	1·6	1·6	—	—	2·8
VII	3·32	3·45	3*e*4*e*	15	1·6	1·6	—	—	2·8
VIII	3·29	3·30	1*e*3*a*4*e*	30	1·5	1·8	—	—	3·0

The C—Cl *Bond Nature*

The fact that the bond moment 2·1 D found at C_4 in IV and V is anomalously large and that 1·4 D at C_3 is small suggests the difference in the contribution from ionic character of the C—Cl bonds. In order to study this postulation, the results of IV and V were compared with those of II, in which the (CC≡N) bond moments are normal. It was found that the 3*p* orbital of Cl atoms, which was the only different point between the chloro- and cyano substituents, clearly plays an important role in the increment of μ (CCl) at C_4 and also in the decrement at C_3. On the other hand, considering the following intermediate, postulated by Bordwell *et al.* for the hydrolysis of chloromethyl arylsulfide,[7]



$$\mathrm{Ar{-}\ddot{\underset{..}{S}}{-}CH_2Cl} \rightarrow [\mathrm{Ar{-}\ddot{\underset{..}{S}}{-}\overset{\oplus}{C}H_2} \leftrightarrow \mathrm{Ar{-}\overset{\oplus}{\underset{..}{S}}{=}CH_2}] + \mathrm{Cl^-}$$

Hydrolysis

it might be expected that the lone pairs locating on the S atom would be important in the increment of μ (CCl) at C_4.

Next the C—Cl bond moments, found in IV and V, were compared with those of VI, VII and VIII. The C—Cl bond moment at C_4 and C_3 of VI and VII, in which lone pairs on the S atom did not remain, were normal; and those of VIII having a lone pair on the S atom lay between those of IV and V and of VI and VII. Seemingly these facts would suggest that the lone pairs on the S atom might be closely related to the increment of μ (CCl) at C_4 and also to the decrement at C_3. On the other hand, from the molecular structures obtained here it could easily be deduced that the interatomic distance (3·0 Å) between S and Cl atoms bonded to C_4 is smaller than the sum of their van der Waals radii (3·7 Å); and that the direction of the chloro substituent at C_4 even in VIII is on the same side as that of the lone pair remaining on the S. In the light of these facts, it can be concluded that the increment of the C—Cl bond moment at C_4 might be due to some interaction between the lone pairs on the S and those on the Cl atoms. Recently, Coulson *et al.*[8] and Bendazzoli *et al.*[9] studied the valence state of the S atom by a theoretical method suggesting that the tetrahedral hydridized orbital (s^2p^3d) is very diffuse and the transition energy from the normal state to the $(s^2p^3)^+$ is very small ($\simeq$1·77 eV). If the divalent state S in the thietane derivatives partially included the (s^2p^3d) state, the transition from the (s^2p^3d) to the $(s^2p^3)^+$ would be favorable stereochemically. On the other hand, an X-ray study of the crystalline complex of Cl and bis(*p*-chlorophenyl)sulfide showed a strong interaction between the Cl atom and the divalent S atom of the molecule.[10] This information supports the conclusion for the interaction between lone pairs of S and Cl atoms. Details of the interaction will be clarified in the future by X-ray studies of these compounds performed in the authors' laboratory.

Temperature dependence of dipole moments

Since a ring-puckering vibration of thietane had been observed by Harris *et al.* from microwave spectra,[11] it was expected that the thietane skeleton of the compounds might have a possibility of puckering motion. Then a temperature dependence of the dipole moments of IV and V should also be observed in the temperature range 25–40°. However no deviation in the dipole moments of these compounds could be found other than experimental errors of measurement in this temperature range.

Acknowledgment—The authors wish to express their gratitude to the Ministry of Education for the Scientific Research Grant which made this work possible.

REFERENCES

[1] A. Ohno, Y. Ohnishi and G. Tsuchihashi, [a] *Tetrahedron Letters* 161 (1969); [b] *J. Am. Chem. Soc.* **91**, 5038 (1969)
[2] C. W. N. Cumper and A. I. Vogel, *J. Chem. Soc.* 3521 (1959)
[3] T. Shimozawa, *Bull. Chem. Soc. Japan* **38**, 1046 (1965)
[4] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.* **64**, 2988 (1942)
[5] M. S. White and B. L. Beeson, Jr., *J. Chem. Phys.* **43**, 1839 (1965)
[6] C–P. Smyth, *Dielectric Behavior and Structure*. McGraw-Hill, New York (1955)
[7] F. G. Bordwell, G. D. Cooper, and H. Morita, *J. Am. Chem. Soc.* **79**, 376 (1957)
[8] C. A. Coulson and F. A. Gianturco, *J. Chem. Soc.* (A), 1618 (1968)
[9] G. L. Bendazzoli and C. Zauli, *J. Chem. Soc.* 6827 (1965)
N. C. Baenziger, R. E. Buckles, R. J. Maner, and T. D. Simpson, *J. Am. Chem. Soc.* **91**, 5749 (1969)
[11] D. O. Harris, H. W. Harrington, A. C. Luntz, and W. D. Gwinn, *J. Chem. Phys.* **44**, 3476 (1966)