QUANTUM CHEMICAL STUDY OF SULFONIUM YLIDES: STRUCTURE, CHARGE DISTRIBUTION AND DIPOLE MOMENTS

Vladimír Král[a], Zdeněk Arnold[a], Václav Jehlička[b] and Otto Exner[a]

[a] *Institute of Organic Chemistry and Biochemistry,*
Czechoslovak Academy of Sciences, 166 10 Prague 6 and
[b] *Department of Physical Chemistry,*
Prague Institute of Chemical Technology, 166 28 Prague 6

The geometry, charge distribution and dipole moments of the parent sulfonium ylide — dimethyl-sulfoniomethylide (*I*) — and a series of stabilized sulfonium ylides, including 2-dimethylsulfuranyl-idene-1,3-cyclopentanedione (*VI*) prepared in this study, was investigated using the CNDO/2, PCILO and *ab initio* methods. Values of dipole moments, calculated by quantum chemical methods (CNDO/2 with the *sp* and *spd* bases, *ab initio* with the STO-3G basis) as well as by the method of empirical bond moments, are compared with the experimental values determined in dioxane or benzene. Dipole moments of several related ammonium ylides were also studied.

Unlike ammonium ylides[1], the known stabilized sulfonium ylides are very numerous thanks to many synthetic ways leading to these compounds. The general synthesis of sulfonium ylides is based on condensation of sulfoxides with compounds, containing an active methylene group, in the presence of various dehydrating agents[2-5]. The reactivity of sulfonium ylides was utilized for the preparation of many other compounds.

Structure of the stabilized sulfonium ylides and charge distribution in them was hitherto determined mainly by spectroscopic methods, particularly by the ^{13}C-NMR spectroscopy[6]. The ^{13}C-signal in the spectra of sulfonium ylides, stabilized by one electronegative group, indicates a marked electron density at the ylide carbon. On the contrary, the ^{13}C-NMR spectra of disubstituted ylides suggest a low electron density, in accord with the experimental behaviour in transylidation and olefin-forming reactions. The ^{13}C-H splitting constant shows an sp^2 hybridisation of the ylide carbon[6]; this agrees with a trigonal planar arrangement found by X-ray studies of various ylides[7-9]. In carbonyl-stabilized sulfonium ylides the shift of the carbonyl carbon signal indicates a significant contribution of the betaine structure, agreeing thus with the found low values of the C=O stretching vibration[1,2].

The IR spectra of carbonyl-stabilized sulfonium ylides exhibit in the region 1 720 to 1 600 cm^{-1} a series of strong bands attributed to conformational non-homogeneity[10]; their relative intensity depends on solvent polarity. The existence of conformational

isomers in these compounds is possible thanks to the higher barrier to rotation around the partially double bond $\overset{(-)}{C}\!=\!C(O)$. In a medium of low dielectric constant, the carbonyl-stabilized sulfonium ylides were shown to exist in the Z,Z-conformers[10]. Also low-temperature ^{1}H-NMR spectra of alkoxycarbonyl-stabilized sulfonium ylides indicate the presence of two rotamers[11]. In the case of dimethyloxy-sulfonioformylmethylide[12] (II), the ^{1}H-NMR spectrum proves directly the existence of two conformers, of which the form with syn-periplanar $\overset{(+)}{S}\!\!-\!\!\overset{(-)}{C}$ and C—O bonds is the predominant one. However, many other carbonyl-stabilized ylides have been found to exist solely in this conformer[12].

Quantum chemical methods (CNDO/2[13] and ab initio[14]) have been hitherto used to calculate the geometry of, and charge distribution in, the simple model molecule of the sulfoniomethylide III. The aim of the present study is to investigate the geometric arrangement of the sulfonium ylides $IV-X$ and the charge distribution in them by the CNDO/2, PCILO and ab initio methods (and to compare the icalculated dipole moments) with the experimental ones. In the study of dipole moments we included also the ammonium ylides $XI-XVI$ which have similar structural features.

The measurements were performed in dioxane and, when the solubility of compounds allowed, also in benzene. However, the accuracy of measurements in benzene was lower and did not improve even by introduction of larger alkyl groups into the molecule (compounds $XII-XIV$) in order to enhance the solubility. Therefore, we took into consideration only the values determined in dioxane, even in cases of compounds, measurable in benzene. We are aware of the fact that a dioxane solution of such strongly polar compounds represents a situation differing considerably from the assumption of isolated molecules; on the other hand, the differences between the dipole moments of the compounds are very expressive and therefore we are of the opinion that a semiquantitative interpretation of the values is reasonable.

EXPERIMENTAL

Melting points were determined on a Kofler block. The analytical samples were dried at 25°C/25 Pa for 24 h over phosphorus pentoxide. The IR spectra were measured on a Zeiss UR 20 spectrometer. The ^{1}H-NMR spectra were taken in deuteriochloroform on Varian HA-100 (100 MHz) and Tesla B 467 (60 MHz) instruments, using tetramethylsilane as internal standard. The UV spectra were measured on a Unicam SP 8000 instrument.

2-Dimethylsulfaranylidene-1,3-cyclopentanedione (VI)

1,3-Cyclopentanedione[15] (0·98 g; 10 mmol) and dicyclohexylcarbodiimide (5·15 g; 25 mmol) were dissolved in a mixture of dimethyl sulfoxide (10 ml) and benzene (10 ml). A 5M solution of anhydrous orthophosphoric acid in dimethyl sulfoxide (1 ml) was then added and the mixture was stirred. After several minutes an exothermic reaction occurred. The mixture was stirred

overnight, diluted with ethyl acetate (50 ml) and the precipitated N,N'-dicyclohexylurea was filtered off. The filtrate was extracted three times with water and the pH value of the combined aqueous extracts was adjusted to 8 by addition of lithium hydroxide solution. After filtration, the solution was taken down, the residue dried (50°C/25 Pa, 1 h) and extracted four times with boiling acetone. Evaporation of the solvent afforded 1·48 g of the crude product, m.p. 180 to 188°C, which was purified by crystallization from acetone at low temperature to give 1·35 g, (86%) of the pure product, m.p. 201—202°C. For $C_7H_{10}O_2S$ calculated: 53·14% C, 6·37% H, 20·26% S; found: 53·25% C, 6·40% H, 20·03% S. ^1H-NMR spectrum (CDCl$_3$, δ): 2·42 s (4 H), 2·99 s (6 H). IR spectrum (CHCl$_3$): ν_s (CH$_3$) 2·942 m, ν_{as} (C$\doteq$O) 1666 m, ν_s (C$\doteq$O) 1604 vs, cm^{-1}. UV spectrum (H$_2$O): λ_{max} 243, ε = 19000; (EtOH): λ_{max} 240, ε = 22300.

Other Ylides

Dimethyl 2-dimethylsulfuranylidenemalonate (*IX*) was prepared in 40% yield similarly as described[2] for the diethyl ester; m.p. 174—175°C (reported[16] m.p. 169—170°C). Dimethylsulfoniodiformylmethylide (*V*) was prepared according to ref.[17]. 2-Dimethylsulfuranylidene-5,5-dimethylcyclohexane-1,3-dione (*VII*), 3-dimethylsulfuranylidene-2,4-pentanedione (*VIII*), and methyl 2-dimethylsulfuranylidenecyanoacetate (*X*) were prepared according to ref.[2]. The ^1H--NMR spectra showed that the described[2] procedure led to compounds, containing N,N'-dicyclohexylurea. Therefore, the products were dissolved in a minimum amount of water and the solution filtered with charcoal. After evaporation of water and drying, the pure compounds were obtained by two crystallizations. The following ammonium ylides for the dipole moment measurements were prepared by the described procedures: trimethylammoniodicyanomethylide[18] (*XI*), butyldimethylammoniodicyanomethylide[19] (*XII*), dimethyloctylammoniodicyanomethylide[19] (*XIII*), dodecyldimethylammoniodicyanomethylide[19] (*XIV*), trimethylammoniodiformylmethylide[20] (*XV*), trimethylammonioacetylcyanomethylide[1] (*XVI*).

Dipole Moment Measurements

Dipole moments of the compounds *IV*—*XVI* were determined in dioxane or benzene solution at 25°C by the method of Halverstadt and Kumler[21]. Usually, five solutions were prepared in the concentration range $2 . 10^{-3}$—$2 . 10^{-2}$M. The permittivity was measured on a heterodyne instrument at 1·2 MHz, the density was determined in an Oswald–Sprengel pycnometer. The dependence of the permittivity ε_{12} and the specific volume d_{12}^{-1} on the weight fraction w_2 did not show any observable curvature and thus there was no indication of dimerisation which, though not unequivocally proved, was assumed for pyridiniumdicyanomethylide[22]. The molar refractivity was calculated using the Vogel increment[23], valid for 20°C; for the atoms of the sulfonium sulfur and ammonium nitrogen we took normal values, derived from sulfides or amines. The resulting error is insignificant in view of high dipole moment values the accuracy of which can be considered to be $0·2 . 10^{-30}$ Cm.

Calculations

The CNDO/2 method was employed in the original parameterisation[24] with the *sp* and *spd* bases. In the PCILO calculations[25] the optimization of bond polarities was carried out in each step and for each conformation. The *ab initio* calculations were executed using the Gaussian 70 program[26] with the STO-3G and 4-31G basis sets[27,28]. These basis sets do not contain the *d*-type functions on second row atoms. Therefore, no conclusion about the significance of the *d*-orbital participation in the compounds can be obtained from these *ab initio* calculations.

Geometric Optimization

The spatial arrangement of the studied ylides was optimized using the CNDO/2 and PCILO methods, the $\overset{(-)(+)}{C-S}$ bond length also by the *ab initio* method. Geometric arrangement of the dimethylsulfonium group in all the studied compounds was taken from the X-ray structure of dimethylsulfoniodicyanomethylide[2,8]. Models of the anion parts of the ylides were optimized by the automatic optimization method using the Derival program[29]. The charge distribution was calculated by the CNDO/2 method (*sp* basis), in the case of several systems (*I, IV, V*) also by the *ab initio* method.

RESULTS AND DISCUSSION

The most important of the calculated bond lengths (Table I), are those of the $\overset{(-)}{C}=C(O,N)$ and $C=O$ or $C\equiv N$ bonds which indicate an extended delocalisation of the charge at the ylide carbon atoms towards the electronegative groups. The $\overset{(-)}{C}=C$ bond is substantially shorter than a common $C_{sp^2}-C_{sp^2}$ bond and also the $C=O$ and $C\equiv N$ bonds are significantly shorter than the standard values. The calculated $\overset{(-)}{C}=C$ and $C=O$ bond lengths can be compared only with few experimental values[8,30] but obviously the CNDO/2 method overestimates the $C=O$ bond length. Closer to the experimental bond lengths are the *ab initio* results (ylide *V*). The $\overset{(-)(+)}{C=S}$ bond lengths, calculated by the semiempirical as well as *ab initio* methods, depend strongly on the type of the AO basis used, particularly on the inclusion of *d*-orbitals[31]. Whereas in ammonium ylides[1] an energy minimum was found for the symmetrical arrangement of the anion part of the molecule, the spatial arrangement of the sulfonium ylides is different. Both calculation and X-ray data[8,30] show an asymmetric arrangement of sulfonium ylides: in the optimum conformation both the methyl groups point to the same oxygen atom (Fig. 1).

The arrangement on the ylide carbon depends on the type of interaction with the adjacent hetero atom. In non-stabilized ammonium ylides we found a pyramidal arrangement on the ylide carbon atom[1], in non-stabilized sulfonium ylides (*I, III*) the result of the CNDO/2 calculation depended on the basis used; the *sp* basis led to the pyramidal ylide carbon whereas the *spd* basis to an approximately planar arrangement. For model ylides (hetero atoms O, S, N, P) it was calculated (*ab initio*, 4-31G basis)[14] that for the second row atoms the carbanion center is more planar and more flexible than for the first row atoms; however, the results of calculations for the non-stabilized ylides cannot be proved experimentally.

In stabilized sulfonium ylides the geometry on the ylide carbon is determined first of all by the conjugative influence of the stabilizing groups. In all stabilized ylides of this type (*IV—X*) we found a planar ylide carbon; this geometry enables

TABLE I

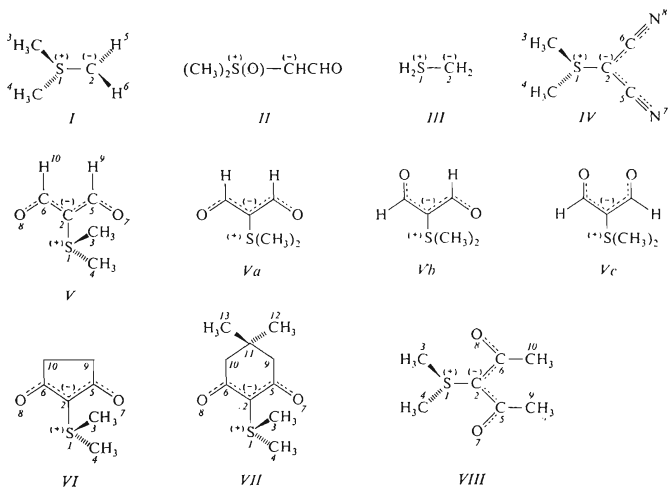Geometric Parameters of the Sulfonium Ylides (CNDO/2, *sp* basis, unless stated otherwise)

Compound	Bond	$r . 10$ (nm)	Bond angle, °		Torsion angle, °	
I	S_1-C_2	$1{\cdot}66^a, 1{\cdot}81^b$	HC_3S_1,	$109{\cdot}5$	$C_3S_1C_2H_6$,	$31{\cdot}2$
		$1{\cdot}80^c$	$H_5C_2H_6$,	120	$C_4S_1C_2H_5$,	$161{\cdot}7$
	$C_2-H_{5,6}$					
III[d]	(+) (−) S_1-C_2	$1{\cdot}801$	HCH,	$109{\cdot}2$	(+) (−) HS_1C_2H,	90
			HSH,	$105{\cdot}4$		
IV[e]	S_1-C_2	$1{\cdot}73$	$C_2S_1C_4$,	$103{\cdot}0$	$C_6C_2S_1C_4$,	$131{\cdot}7$
	C_2-C_6	$1{\cdot}41$	$C_2S_1C_3$,	$107{\cdot}3$		
	C_2-C_5	$1{\cdot}395$	$C_3S_1C_4$,	$101{\cdot}7$		
	C_5-N_7	$1{\cdot}167$	$S_1C_2C_5$,	$119{\cdot}3$	$C_5C_2S_1C_3$,	$61{\cdot}2$
	C_6-N_8	$1{\cdot}158$	$S_1C_2C_6$,	$118{\cdot}3$		
	S_1-C_3	$1{\cdot}81$	$C_2C_6N_8$,	$179{\cdot}0$		
	S_1-C_4	$1{\cdot}841$	$C_2C_5N_7$,	$177{\cdot}2$		
	$C{\equiv}N^f$	$1{\cdot}195$				
V	S_1-C_2	$1{\cdot}71^a, 1{\cdot}81^b$	$S_1C_2C_{5,6}$,	$116{\cdot}8$	$C_6C_2S_1C_4$,	$131{\cdot}7$
		$1{\cdot}80^c, 1{\cdot}795^g$	$C_2C_5O_7$,	$128{\cdot}6$		
			$C_2C_5H_9$,	$119{\cdot}6$	$C_5C_2S_1C_3$,	$61{\cdot}2$
	C_2-C_5	$1{\cdot}395^{b,g}$				
	C_2-C_6	$1{\cdot}410^{b,g}$				
	C_5-O_7	$1{\cdot}284^b, 1{\cdot}255^g$				
	C_5-H_9	$1{\cdot}12^b, 1{\cdot}09^g$				
VI[i]	S_1-C_2	$1{\cdot}71^a$	$S_1C_2C_5$,	$124{\cdot}1$	$S_1C_2C_5O_7$,	0
		$1{\cdot}80^b$	$C_2C_5O_7$,	$129{\cdot}0$		
	C_2-C_5	$1{\cdot}419$	$C_2C_5C_9$,	$107{\cdot}0$	$S_1C_2C_5C_9$,	180
	C_5-O_7	$1{\cdot}28$	$C_5C_9C_{10}$,	$107{\cdot}1$		
	C_5-C_9	$1{\cdot}48$				
	C_9-C_{10}	$1{\cdot}482$				
VII[b]	S_1-C_2	$1{\cdot}81^b$	$C_1C_2C_5$,	$120{\cdot}0$	$C_2C_5C_9C_{11}$,	$25{\cdot}8$
	C_2-C_5	$1{\cdot}412$	$C_2C_5C_9$,	$120{\cdot}2$	$C_5C_9C_{11}C_{12}$,	180
	C_5-O_7	$1{\cdot}28$	$C_2C_5C_7$,	$126{\cdot}5$	$C_5C_9C_{11}C_{13}$,	60
	C_5-C_{11}	$1{\cdot}480$	$C_5C_9C_{11}$,	$110{\cdot}4$		
	C_9-C_{11}	$1{\cdot}515$				
	$C_{11}-C_{13}$	$1{\cdot}520$				
IX	C_2-C_5	$1{\cdot}400$	$S_1C_2C_5$,	$117{\cdot}4$	$S_1C_2C_5O_7$,	0
	C_2-C_6	$1{\cdot}420$	$C_2C_5O_7$,	$123{\cdot}2$	$S_1C_2C_5O_9$,	180
	C_5-O_7	$1{\cdot}275$	$C_2C_5O_9$,	$122{\cdot}1$		
	C_5-O_9	$1{\cdot}33$	$C_5O_9C_{11}$,	$118{\cdot}3$		

TABLE I
(Continued)

Compound	Bond	$r \cdot 10$ (nm)	Bond angle, °		Torsion angle, °	
X	S_1—C_2	$1 \cdot 72^a$	$S_1C_2C_5$,	$116 \cdot 0$	$S_1C_2C_5O_7$,	0
	C_2—C_5	$1 \cdot 400$	$S_1C_2C_6$,	$114 \cdot 0$	$S_1C_2C_5O_9$,	180
	C_2—C_6	$1 \cdot 41$	$C_2C_6N_8$,	$179 \cdot 0$	$S_1C_2C_6N_8$,	0
	C_5—O_7	$1 \cdot 275$	$C_5O_9C_{10}$,	$118 \cdot 3$		
	C_5—O_9	$1 \cdot 32$				
	C_6—N_8	$1 \cdot 19$				

^{a} CNDO/2, spd basis; ^{b} CNDO/2, sp basis; ^{c} PCILO; ^{d} ab initio 4—31G, ref.[14]; ^{e} X-ray, ref.[8]; ^{f} value obtained by calculation (CNDO/2, sp), other values identical with those of X-ray; ^{g} ab initio STO-3G; ^{i} optimization for compounds VI and VII carried out assuming a symmetrical arrangement of the ring relative to the axis lying in the S—C bond.

the greatest extent of the charge transfer towards the stabilizing groups. The X-ray studies on stabilized ylides[8],[30] confirm this conclusion.
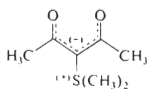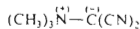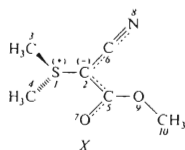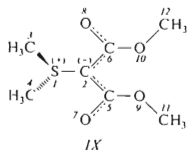

I   *II*   *III*   *IV*

V   *Va*   *Vb*   *Vc*

VI   *VII*   *VIII*

VIIIa   *VIIIb*   *VIIIc*

IX   *X* $(CH_3)_3\overset{(+)}{N}-\overset{(-)}{C}(CN)_2$

                 XI

$C_4H_9(CH_3)_2\overset{(+)}{N}-\overset{(-)}{C}(CN)_2$ $C_8H_{17}(CH_3)_2\overset{(+)}{N}-\overset{(-)}{C}(CN)_2$ $C_{12}H_{25}(CH_3)_2\overset{(+)}{N}-\overset{(-)}{C}(CN)_2$

     XII   *XIII*   *XIV*

$(CH_3)_3\overset{(+)}{N}-\overset{(-)}{C}(CHO)_2$ $(CH_3)_3\overset{(+)}{N}-\overset{(-)}{C}(CN)COCH_3$
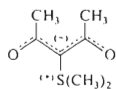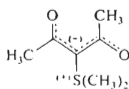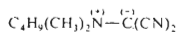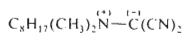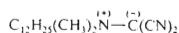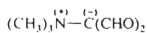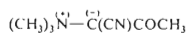
     XV   *XVI*

The charge distributions in sulfonium ylides are summarized in Table II and III. In the non-stabilized ylides *I, III* the predominant part of the negative charge is concentrated on the ylide carbon which has a marked carbanion character. On the contrary, the charges and bond orders in stabilized ylides indicate a significant
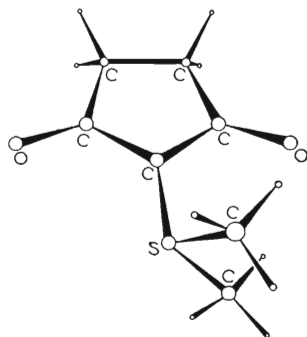
Fig. 1

Spatial Arrangement of 2-Dimethylsulfur-anylidene-1,3-cyclopentanedione (*VI*)

transfer of the negative charge to the electronegative atoms of the stabilizing groups. This conclusion agrees with the calculated arrangement on the ylide carbon, with the calculated $C \doteq C$ and $C—X$ ($X = O$, N) bond lengths and also with the reactivity of these compounds. Also the abnormally low carbonyl stretching vibration value in 3-carbonyl-stabilized ylides[1,2,17,20,32] shows the importance of the charge delocalisation towards oxygen. Contrary to ammonium ylides[1], the charge distribution is not symmetrical. A greater part of the negative charge is localized at the carbonyl group the oxygen atom of which is closer to the positively charged hydrogen atoms of the dimethylsulfonium group. The charge distribution values, calculated by the *ab initio* and CNDO/2 methods give the same picture concerning the electron density in these molecules, differing more significantly only in the charges, calculated for the carbon atoms of the dimethylsulfonium group. The significance of the *d*-orbital participation in this type of compounds is discussed in ref.[31].

ylide form   betaine form
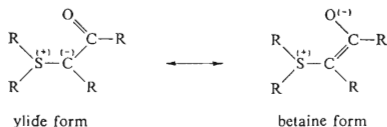
An experimental proof of the calculated charge distribution can be obtained first of all from dipole moment values. We shall turn our attention first to the compounds *IV*, *VI* and *VII* (Table IV) whose conformation is unequivocal. The comparison of calculated and experimental dipole moment values is not so simple as it has been in the case of the ammonium ylides[1]: first, the experimental values are strongly solvent-dependent (see compounds *VI* and *VII*) and for technical reasons they cannot be measured in a less polar medium; second, the calculated values depend substantially on the AO basis used. For sulfonium ylides, this latter dependence is more marked than for other types of sulfur compounds. Inclusion of 3*d* orbitals in the basis set leads to a reduction of the charges[31] on the S—C bond and thus to a significant decrease in the calculated dipole moments. Dipole moments calculated with the *sp* basis are usually higher than the experimental values, whereas those calculated with the *spd* basis are lower, although the latter agree fairly well with the values found in benzene, if available. The *ab initio* calculations led in two cases to distinctly too high dipole moments. For a good description, the inclusion of the *d* orbitals for sulfonium ylides would obviously be necessary because in the case of ammonium bases the STO-3G basis gave very good results[1].

Let us consider the conformation of stabilized sulfonium ylides. Sufficient evidence has been presented to prove the existence of conjugation of the carbonyl groups

TABLE II

Charge Distribution in Sulfonium Ylides (CNDO/2, sp basis)

Compound	Atom A	Q_A	Bond	W_{A-B}
I	S_1	0·349	S_1—C_2	0·792
	C_2	−0·379	S_1—C_3	0·977
	C_3	−0·028	S_1—C_4	0·971
	C_4	−0·024	C_2—H_5	0·979
	H_5	−0·052	C_2—H_6	0·983
	H_6	−0·043	C_3—H	0·99
	$H_3(C)$	0·02−0·04		
IV	S_1	0·316	S_1—C_2	0·741
	C_2	−0·231	S_1—C_3	0·972
	C_3	−0·019	S_1—C_4	0·972
	C_4	−0·013	C_2—C_5	1·225
	C_5	0·098	C_2—C_6	1·199
	C_6	0·105	C_5—N_7	2·704
	N_7	−0·261	C_6—N_8	2·729
	N_8	−0·249	C_3—H	0·99
	$H_3(C)$	0·02−0·06		
V	S_1	0·403	S_1—C_2	0·750
	C_2	−0·198	S_1—C_3	0·974
	C_3	−0·010	S_1—C_4	0·975
	C_4	−0·013	C_2—C_5	1·321
	C_5	0·250	C_2—C_6	1·275
	C_6	0·252	C_5—H_9	0·914
	O_7	−0·407	C_5—O_7	1·658
	O_8	−0·377	C_6—O_8	1·701
	H_9	−0·041	C_6—H_{10}	0·916
	H_{10}	−0·037	C_4—H	0·99
	$H_3(C)$	0·03−0·08		
VI	S_1	0·293	S_1—C_2	0·745
	C_2	−0·225	C_2—C_5	1·251
	C_6	0·261	C_2—C_6	1·238
	C_5	0·255	C_5—O_7	1·602
	O_7	−0·428	C_6—C_8	1·611
	O_8	−0·414	C_5—O_9	1·007
	C_9	−0·016	C_9—C_{10}	1·025

TABLE II

(*Continued*)

Compound	Atom A	Q_A	Bond	W_{A-B}
VII	S_1	0·301	S_1-C_2	0·749
	C_2	−0·221	C_2-C_5	1·274
	C_5	0·253	C_2-C_6	1·260
	O_7	−0·435	C_9-C_{11}	0·975
	O_8	−0·419	C_5-O_7	1·587
	C_9	−0·020	C_5-C_9	1·007
	C_{11}	0·056		
	C_{13}	−0·011	C_6-O_8	1·605
IX	S_1	0·330	S_1-C_2	0·797
	C_2	−0·266	C_2-C_5	1·241
	C_5	0·399	C_2-C_6	1·226
	C_6	0·403	C_5-O_7	1·564
	O_7	−0·480	C_5-O_9	1·040
	O_8	−0·464	O_9-C_{11}	0·989
	O_9	−0·223	C_6-O_8	1·585
	O_{10}	−0·224	C_6-O_{10}	1·037
	C_{11}	0·139	$O_{10}-C_{12}$	0·988
	C_{12}	0·139		
X	S_1	0·282	S_1-C_2	0·729
	C_2	−0·241	C_2-C_5	1·255
	C_5	0·393	C_2-C_6	1·240
	C_6	0·053	C_5-O_7	1·550
	O_7	−0·474	C_5-O_9	1·036
	N_8	−0·182	C_6-N_8	2·691
	O_9	−0·225	O_9-C_{10}	0·989
	C_{10}	0·141		

with the central S—C bond and therefore we may assume only coplanar conformations. We thus consider three forms (Z,Z, E,Z and E,E) for the compounds *V*, *VIII* and *IX* (e.g. *Va − Vc*), and two forms (Z and E) for the compound *X*. From our data, the conformational population can be derived in three ways: *a*) by direct comparison of the energies calculated for the single conformers; *b*) from the experimental dipole moments by classical analysis in terms of bond moments; *c*) by comparison of experimental values with dipole moments, calculated by quantum chemical methods. The direct calculation of the total energy was performed for all the mentioned com-

Table III

Calculated (*ab initio*) Gross Atomic Charges in Sulfonium Ylides

Compound	Atom	Q (a.u.)	Compound	Atom	Q (a.u.)
I	S_1	0·464		C_3	−0·245
	C_2	−0·424		C_4	−0·257
	C_3	−0·254		C_5	0·041
	C_4	−0·260		C_6	0·057
	H_5	−0·044		N_7	−0·266
	H_6	−0·036		N_8	−0·261
	$H_3(C)$	0·08 − 0·10			
			V	S_1	0·509
III[a]	S_1	0·150		C_2	−0·246
	C_2	−0·699		C_3	−0·259
	H_C	0·12, 0·13		C_4	−0·255
	H_S	0·12, 0·14		C_5	0·083
				C_6	0·088
IV	S_1	0·540		O_7	−0·346
	C_2	−0·269		O_8	−0·314
				H_9	0·043
				H_{10}	0·040

[a] 4−31G Basis, ref.[14], net atomic charges.

Table IV

Comparison of Found and Calculated Dipole Moments of Sulfonium Ylides

Compound	μ_{calc} (Cm . 10^{-30})			μ_{exp} (Cm . 10^{-30}) (dioxane)
	CNDO/2 (*sp*)	CNDO/2 (*spd*)	*ab initio*[a]	
IV	31·1	22·3	32·1	16·9[b]
V	16·2	11·7	17·5	15·1
VI	16·0	10·8		18·2; 12·7[c]
VII	14·5	10·3		12·1; 10·7[c]
IX	17·8	12·7		14·4
X	23·4	17·9		20·4

[a] STO-3G Basis; [b] ref.[2]; [c] determined in benzene.

pounds by the CNDO/2 method. The best conformations in terms of energy proved to be the Z,Z form for V and IX, and the Z conformation for the compound X; in all cases these most stable conformations were by at least 12·5 kJ mol^{-1} more stable than the alternative conformation E,Z or E. The barrier to transition to the E,Z conformer in the ylide V was calculated to be 133 kJ mol^{-1} (CNDO/2). Thus, all these compounds appear to be conformationally homogeneous. Another situation, however, was found with the ylide $VIII$. In this case the E,Z conformer ($VIIIb$) was found to be the most stable but it differs by only 2·8 kJ mol^{-1} from the Z,Z conformer ($VIIIa$). This energy difference corresponds to 75% of $VIIIb$ and 25% of $VIIIa$ at 298 K. Another argument for the presence of two conformers at equilibrium are two maxima in the electronic spectrum (λ 231 nm, ε 10460 and λ 269 nm, ε 13530)[2]; other sulfonium ylides, studied in this work exhibit only one maximum[2,17].

The classical analysis of experimental dipole moments requires an approximate calculation of the expected values for the single conformations by vector addition of constant bond moments[33]. However, the studied compounds exhibit a considerable charge delocalisation and therefore standard bond moments could afford only very crude values. In a better approximation, it is possible to introduce empirical mesomeric corrections in the form of vectors, expressing the direction and magnitude of the charge transfer as compared with the classical structure[33]. In our case we can formally include these corrections into the bond moment of the strongly polar $\overset{(+)\ (-)}{\text{S—C}}$ bond which, anyway, is not known as such; this procedure is justified at least for symmetrical molecules in symmetrical conformations. In any case, the bond moment of the $\overset{(+)\ (-)}{\text{S—C}}$ bond has naturally no physical meaning and cannot be expected to be constant for all the compounds. Moreover, it involves also the negatively taken moment of the lone electron pair of the sulfur atom which is inherently present[33] in the C—S bond moment. Its, probably overestimated[34], value can be determined only by theoretical calculations; in compounds $IV-X$ it will be nearly constant. If we start from the experimental dipole moments of the conformationally rigid molecules VI and VII, and subtract the standard bond moments[33] for all the other bonds, we obtain for the $\overset{(+)\ (-)}{\text{S—C}}$ bond the respective values 22·0 and 19·5 . 10^{-30} Cm (the bond angles were taken from Table I). As expected, the agreement between these two values is only approximate. Nevertheless, the mean value (20·7) can be taken as an approximation in dipole moment calculations for single conformations of carbonyl-stabilized ylides. Thus, in the case of V we obtain for the respective Z,Z, Z,E, E,Z and E,E conformations the following values: 16·7, 27·5, 29·4 and 39·3 (. 10^{-30} Cm); for the compound IX the respective values are 17·2, 24·9, 26·4 and 33·5 (. 10^{-30} Cm). (The Z,E conformation differs from the E,Z form in the relation between the carbonyl oxygen and methyl groups on the sulfur atom.) Regardless of the much approximative character of the whole calculation, in both cases the experimental value speaks

unequivocally in favour of the Z,Z form, the decisive factor being magnitude of the C=O bond moment. In accord with the quantum chemical calculations, the compound *VIII* is obviously conformationally not homogeneous. The calculated values are 14·7, 27·1, 29·3 and 40·5 . 10^{-30} Cm for the respective above-mentioned conformers, the experimental dipole moment being 20·2 (Table V). The ratio of conformers can be only very roughly estimated to be 1 : 1 if we prefer the experimental value in dioxane because our values refer to this solvent. For the compound *X* we must consider, in addition to the two conformations (E and Z) of the acetyl group, rotamers around the S—C bond, ranging from the *sc* to *ac* relation between the methyl and carbomethoxyl groups. The moment (20·7) of this bond, derived from ketones, is obviously too high. We chose the value of 16·7 which is an approximate

TABLE V
Experimental Dipole Moments of the Sulfonium and Ammonium Ylides *IV— XVI*

Compound	Solvent	P_2^o, cm³	R_D, cm³	$\mu(5)^a$ 10^{-30} Cm	$\mu(15)^a$ 10^{-30} Cm
IV	dioxane	—	—	26·9[b]	—
	benzene	—	—	24·7[c]	—
V	dioxane	467·5	33·5	15·2	15·1
VI	dioxane	654·5	40·2	18·2	18·1
	benzene	344·0	40·2	12·8	12·7
VII	dioxane	331·3	54·2	12·2	12·1
	benzene	274·9	54·2	10·8	10·7
VIII	dioxane	795·1	42·7	20·2	20·1
	benzene	536·2	42·7	16·3	16·2
IX	dioxane	431·5	45·6	14·4	13·3
X	dioxane	813·9	39·2	20·5	20·4
XI	dioxane	1 405	33·3	27·3	27·2
XII	dioxane	1 618	47·2	29·2	29·1
XIII	dioxane	1 636	65·8	29·2	29·1
XIV	dioxane	1 724	94·4	29·8	29·7
XV	dioxane	524·0	34·0	16·3	16·2
XVI	dioxane	830·6	38·3	20·7	20·6

[a] Correction for atomic polarisation: 5% or 15% of the R_D value; [b] ref.[2]; [c] ref.[34].

mean of the values derived from bromo ketones $(20 \cdot 0$ or $19 \cdot 5 \cdot 10^{-30}$ Cm) and from the dinitrile $IV (13 \cdot 0 \cdot 10^{-3}$ Cm). The respective calculated values are then $21 \cdot 5$, $24 \cdot 0$, $30 \cdot 3$ and $33 \cdot 3$ for the Z,sc; Z,ac, E,sc and E,ac conformation. The conformational assignment to the carbomethoxy group is again unequivocal, in spite of the considerably approximate calculation; in the most probable position of the dimethylsulfonium group the methyl groups are close to the carbonyl.

The spatial arrangement of stabilized ammonium ylides has been already studied in our Laboratory by physico-chemical (NMR, IR) (ref.[35]) as well as quantum chemical methods[1,36], the result being an unequivocal assignment of the Z,Z conformation to carbonyl-stabilized ylides. For an analysis of dipole moments of these compounds, based on empirical bond moments, no conformationally fixed model compounds are available. Nevertheless, using this procedure, we can prove the Z,Z conformation in the dialdehyde XV if in the calculation we use for the $\overset{(+)}{N}—\overset{(-)}{C}$ bond an approximate moment derived from the dinitrile XI.

The third method of conformational assignment, based on dipole moments calculated by quantum chemical methods, is — contrary to the case of ammonium ylides[1] — complicated by the choice of a suitable AO basis for the dipole moment calculation (Table IV). This approach was investigated in more detail with the ylide V, for which the calculated dipole moments (CNDO/2, sp basis) for the Z,Z, E,Z, and E,E conformations are $16 \cdot 2$, $27 \cdot 4$ and $44 \cdot 0 \cdot 10^{-30}$ Cm, respectively. As seen, the decision is unequivocal.

The results of all the three approaches, used for the determination of conformation of the stabilized ylides, are in a good accord. Obviously, the steric arrangement of the studied compounds is determined decisively by the electrostatic repulsion between the carbonyl oxygens, and, simultaneously, by the attraction between the positively charged atoms of the dimethylsulfonium or trimethylammonium groups and the negatively charged carbonyl oxygens.

REFERENCES

1. Král V., Arnold Z.: This Journal **45**, 92 (1980).
2. Cook A. F., Moffatt J. G.: J. Amer. Chem. Soc. **90**, 740 (1968).
3. Hochrainer A., Wessely F.: Tetrahedron Lett. *1965*, 721.
4. Schank K., Schuhknecht C.: Synthesis *1978*, 678.
5. Nozaki H., Morita Z., Kondo K.: Tetrahedron Lett. *1966*, 2913.
6. Matsuyama H., Minato H., Kobayashi M.: Bull. Chem. Soc. Jap. **50**, 3393 (1977).
7. Baezinger N. C., Foster B. A., Howels H., Howels R., Van der Valk P., Burton D. J.: Acta Crystallogr. Sect. B **33**, 2327 (1977).
8. Christensen A. T., Whitmore W. G.: Acta Crystallogr. Sect. B **25**, 73 (1969).
9. Schaefer J. P., Reed L. L.: J. Amer. Chem. Soc. **94**, 908 (1972).

10. Boldeckul I. E., Loktionova R. A., Repina L. A., Lysenko V. Z.: Zh. Obshch. Khim. 47, 2735 (1977).
11. Casanova J. jr, Rutolo D. A. jr: Chem. Commun. 1967, 1224.
12. Kondo K., Tunemoto D.: Chem. Commun. 1970, 1361.
13. Tatsumi K., Yoshioka Y., Yamaguchi K., Fueno T.: Tetrahedron 32, 1705 (1976).
14. Bernardi F., Schlegel M. B., Whangbo M., Wolfe S.: J. Amer. Chem. Soc. 99, 5633 (1977).
15. Sraza J., Hrnčiar P.: Z. Chem. 1975, 188.
16. Ando W., Yagihara T., Tozune S., Toshihiko M.: J. Amer. Chem. Soc. 91, 2786 (1969).
17. Král V., Arnold Z.: This Journal 43, 1248 (1978).
18. Arnold Z.: Chem. Ind. (London) 1960, 1478; This Journal 26, 1113 (1961).
19. Svoboda M., Vašíčková S., Arnold Z.: This Journal 43, 1254 (1978).
20. Král V., Arnold Z.: This Journal 42, 3455 (1977).
21. Halverstadt L. F., Kumler W. D.: J. Amer. Chem. Soc. 64, 2988 (1942).
22. Treiner C., Skinner J. F., Fuoss R. M.: J. Chem. Phys. 68, 3406 (1964).
23. Vogel A. I.: J. Chem. Soc. 1948, 1842.
24. Pople J. A., Beveridge D. L.: *Approximate Molecular Orbital Theory*. McGraw-Hill, New York 1970.
25. Claverie P., Daudey J. P., Diner S., Geissner-Prettre G., Gilbert M., Langlet L., Malrieu J. P., Pincelli U., Pullman B.: Quantum Chemistry Program Exchange No 220/221, Bloomington, Indiana, USA.
26. Hehre W. J., Lathan W. A., Ditchfield R., Newton M. D., Pople J. A.: Gaussian 70, No 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana, USA.
27. Ditchfield R., Hehre W. J., Pople J. A.: J. Chem. Phys. 54, 724 (1971).
28. Hehre W. J., Lathan W. A.: J. Chem. Phys. 56, 5255 (1972).
29. Pancíř J.: This Journal 40, 1112 (1975).
30. Christensen A. T., Thorn E.: Acta Crystallogr. Sect. B. 27, 581 (1971).
31. Král V.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1977.
32. Trost B. M.: J. Amer. Chem. Soc. 89, 138 (1967).
33. Exner O.: *Dipole Moments in Organic Chemistry*, Chapter 3.3. Thieme, Stuttgart 1975.
34. Goetz H., Klabuhn B., Marschner F., Hohberg H., Skuballa W.: Tetrahedron 27, 999 (1971).
35. Svoboda M., Synáčková M., Samek Z., Fiedler P., Arnold Z.: This Journal 43, 1261 (1978).
36. Král V., Arnold Z.: This Journal 45, 80 (1980).

Translated by M. Tichý.