

## STUDY OF SOME ALIPHATIC AMMONIUM YLIDES BY SEMIEMPIRICAL AND *ab initio* METHODS: STRUCTURE AND CHARGE DISTRIBUTION

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Structure of, and charge distribution in, some aliphatic ammonium ylides were determined by quantum chemical methods (CNDO/2, INDO, MINDO/2, PCIL0, *ab initio*-STO-3G and 4-31G bases). Non-stabilized ylides were found to have pyramidal arrangement of bonds on the ylide carbon whereas the stabilized ylides have a planar arrangement. The charge distribution in stabilized ylides indicates a significant transfer of the negative charge from the ylide carbon to the electronegative groups. The calculated dipole moments for the previously prepared compounds, as well as for the derivatives *VII* and *X*, described in this paper, agree well with the experimental value.

The present paper summarises the results of our investigations on aliphatic ammonium ylides. The aim of our work was to compare geometric parameters and charge distribution in ammonium ylides *I* and their dependence on the electronic character of the groups  $R^2$  and  $R^3$ . Non-stabilized ammonium ylides react as common carbanions ( $R^2 = R^3 = H$  or alkyl). Ammonium ylides, stabilized with one electronegative group, retain their nucleophilic properties<sup>1</sup>. If two clearly electronegative groups are bonded to the ylide carbon, the compound does not exhibit nucleophilic properties and loses its carbanion character<sup>2,3</sup>.

From the quantum chemical point of view, only model systems of ylide compounds have been hitherto studied. Greatest attention has been paid to the nature of the bond between the hetero atom and the ylide carbon and to the geometric arrangement of phosphoniomethylide<sup>4-6</sup> (*II*) and sulfoniomethylide<sup>7</sup> (*III*). The American authors who studied a whole series of model ylides<sup>8</sup> (hetero atom P, S, N, O) using the *ab initio* method (4-31G basis) investigated also ammoniomethylide (*IV*) and determined its geometric arrangement and charge distribution in this compound. Dewar and coworkers<sup>9</sup>, in connection with a study of stereochemical aspects of Stevens rearrangement, investigated the structure of trimethylammoniomethylide (*V*) and trimethylammoniobenzoylmethylide (*VI*) and calculated their optimal geometric arrangement by the MINDO/3 method<sup>9</sup>.

We have extended the existing knowledge by investigation of the geometry of, and charge distribution in, trimethylammoniomethylide (*V*) and a series of stabilized ammonium ylides by non-empirical and semiempirical methods. Two new compounds (*VII* and *X*) were added to the series of known ylides, studied in this work. The ylide *VII*, stabilized with two ester groups, was prepared by standard reactions from methyl malonate. Its bromination, followed by reaction with dimethylamine, afforded the dimethylamino derivative *VIII*, which was quaternised with methyl iodide to give the salt *IX* from which the desired product *VII* was obtained by elimination of hydrogen iodide. Synthesis of the derivative *X* started from trimethylammoniodicyanomethylide (*XI*), described previously. On treatment with Grignard reagent, only one cyano group in this compound reacts under formation of trimethylammonioacetylcyanomethylide (*X*) as the end product.

## EXPERIMENTAL

Melting points were determined on a Kofler block. The analytical samples were dried over phosphorus pentoxide at 25°C/27 Pa for 24 h. IR spectra were measured on a Zeiss UR 20 spectrometer, <sup>1</sup>H-NMR spectra on a Varian HA-100 (100 MHz) instrument in deuteriochloroform with tetramethylsilane as internal standard. UV spectra were taken on a Unicam SP 8000 spectrometer.

### Dimethyl Dimethylaminomalonate (*VIII*)

The title compound was prepared analogously as described for the corresponding diethyl ester<sup>10</sup>. A solution of dimethylamine (18 g; 0.4M) in methanol (50 ml) was added dropwise to a solution of dimethyl bromomalonate<sup>11</sup> (43 g; 0.2M) in methanol (50 ml) and then heated to 60°C for 1 h. Ether (100 ml) was added to the mixture and the precipitated dimethylamine hydrobromide filtered off. After removal of the solvent on a rotatory evaporator the residue was distilled affording 27 g (76%) of the product, boiling at 98–100°C/2.0 kPa. Prior analysis the compound was distilled through a column, the fraction b.p. 98–99°C/2.0 kPa being taken. For C<sub>7</sub>H<sub>13</sub>NO<sub>4</sub> (175.2) calculated: 47.99% C, 7.48% H, 8.00% N; found: 47.76% C, 7.40% H, 7.93% N.

### (Dimethyl Trimethylammoniomalonate) Iodide (*IX*)

Methyl iodide (4.26 g) was added with stirring to the compound *VIII* (1.75 g; 10 mm). The mixture was cooled with ice-water for 20 min and set aside for 5 h at room temperature. After addition of ether (50 ml) the product was filtered; yield 2.85 g (90%), m.p. 129°C. For C<sub>8</sub>H<sub>16</sub>INO<sub>4</sub> (317.1) calculated: 30.29% C, 5.09% H, 40.02% I, 4.42% N; found: 29.88% C, 5.18% H, 40.57% I, 4.59% N.

### Trimethylammonio-bis(methoxycarbonyl)methylide (*VII*)

Silver oxide (2.32 g; 10 mm) was added portionwise to a solution of the compound *IX* (1.586 g; 5 mm) in acetonitrile (20 ml) and the mixture was stirred for 30 min. After filtration, the filtrate was taken down, the solid dissolved in dichloromethane, the solution treated with charcoal, filtered and taken down. The product was crystallized from tetrachloromethane-cyclohexane

(1 : 1), m.p. 131–133°C; yield 0.91 g (96%). For  $C_8H_{15}NO_4$  (189.2) calculated: 50.78% C, 7.99% H, 7.40% N; found: 50.62% C, 7.92% H, 7.65% N.  $^1H$ -NMR spectrum ( $CDCl_3$ ,  $\delta$ ): 3.49 s (9 H), 3.58 s (6 H); IR spectrum (KBr,  $cm^{-1}$ ):  $\nu_{as}(CH_3)$  3049 m, 3018;  $\nu(C=O)$  1636 vs, 1599 s, s. IR spectrum ( $CHCl_3$ ,  $cm^{-1}$ ):  $\nu(C=O)$  1646, 1602 vs;  $\delta_{as}(CH_3)$  [ $N^+$ ] 1496 m. UV spectrum (EtOH):  $\lambda_{max}$  253,  $\epsilon$  394.

#### Trimethylammonioacetyl cyanomethylide (X)

A 2N methylmagnesium iodide solution (25 ml; 50 mmol) in ether was added to a solution of crystallized and dried trimethylammoniodicyanomethylide (XI; 0.615 g; 5 mmol) in 1,2-dimethoxyethane (30 ml). The ether was distilled off and the mixture heated for 6 h to 60°C. After cooling the solution was poured on ice (50 g) and conc. hydrochloric acid was added with stirring. The organic solvent was driven off on a rotatory evaporator and the mixture was kept at 80°C for 15 min. After cooling the mixture was saturated with potassium carbonate and extracted with a benzene-ethanol (2 : 1) mixture (5 × 50 ml). The combined extracts were dried, filtered with charcoal and taken down. The residue was dissolved in chloroform, the solution taken down on a rotatory evaporator and the product crystallized from benzene, m.p. 205–207°C; yield 0.42 g (60%). For  $C_7H_{12}N_2O$  (140.2) calculated: 59.97% C, 8.63% H, 19.99% N; found: 60.02% C, 8.55% H, 20.21% N.  $^1H$ -NMR spectrum ( $CDCl_3$ ,  $\delta$ ): 2.01 s (3 H); 3.43 s (9 H); IR spectrum ( $CHCl_3$ ),  $cm^{-1}$ :  $\nu_{as}(CH_3)$  3057;  $\nu(C\equiv N)$  2163, 2132;  $\nu(C=O)$  1570, 1557, 1533 sh;  $\delta_{as}(CH_3)$  [ $N^+$ ] 1489, 1468;  $\delta_s(CH_3)$  [ $N^+$ ] 1439, 1401;  $\delta_s(CH_3)$  [C] 1381. IR spectrum (KBr,  $cm^{-1}$ ):  $\nu_{as}(CH_3)$  3065, 3045;  $\nu(C\equiv N)$  2177 sh, 2150, 2125, 2038,  $\nu(C=O)$  1574, 1557 sh, 1539 sh;  $\delta_{as}(CH_3)$  [ $N^+$ ] 1495, 1470,  $\delta_s(CH_3)$  [ $N^+$ ] 1426, 1392,  $\delta_s(CH_3)$  [C] 1374. UV spectrum (EtOH):  $\lambda_{max}$  247,  $\epsilon$  15510.

#### Calculations

The CNDO/2, INDO (ref.<sup>12,13</sup>) and MINDO/2<sup>14</sup> methods were employed using the original parameterisation. In the PCILO (ref.<sup>15</sup>) calculations the optimization of the bond polarities was carried out in each step and for each conformation. The *ab initio* calculations were performed using the Gaussian 70 program<sup>16</sup> and the STO-3G and 4-31G basis sets<sup>17,18</sup>.

#### Geometric Optimization

The spatial arrangement of the studied ylides was optimized by the CNDO/2 and PCILO methods under assumption of a tetrahedral trimethylammonium group with standard bond lengths and angles<sup>19</sup> ( $r_{C-N}$  0.147 nm,  $r_{C-H}$  0.109 nm,  $\angle NCH$  109.47°). The character and length of the (-)(+)

C–N bond was estimated, in addition to the semiempirical methods (CNDO/2, INDO, MINDO/2, PCILO), also by the *ab initio* method. The charge distribution was studied by the CNDO/2, INDO and MINDO/2 methods and the results were compared with those obtained by the *ab initio* methods in the STO-3G and 4-31G bases.

## RESULTS AND DISCUSSION

The geometric arrangement and charge distribution were studied on the systems IV, V, VII, X, XI and XII. The optimized bond lengths, and the bond and dihedral angles in the most stable conformations are summarized in Tables I and II. The spatial arrangement of the ylides VII and X is depicted in Fig. 1 and 2.

(-) (+) (-) (+)

*Length of the C—N bond:* The hitherto experimentally determined C—N bond lengths, together with the calculated values, are given in Table I. It is evident that the results of the *ab initio* method differ from those of some semiempirical methods.

TABLE I  
(+) (-)  
N—C Bond Lengths for the Series of Ammonium Ylides

Compound	Method	r. 10, nm	Compound	Method	r. 10, nm
IV	<i>ab initio</i> (4-31G)	1.538 <sup>a</sup>	VII	CNDO/2	1.455
	CNDO/2	1.425	X	CNDO/2	1.452
	INDO	1.430	XI	CNDO/2	1.450
	MINDO/2	1.470	XII	<i>ab initio</i> (STO-3G)	1.530
V	<i>ab initio</i> (STO-3G)	1.535		CNDO/2	1.450 <sup>c</sup>
	MINDO/3	1.471 <sup>b</sup>		PCILO	1.475
	PCILO	1.475	XIII	X-ray	1.464 <sup>d</sup>
	CNDO/2	1.430	XIV	X-ray	1.47 <sup>c</sup>
	INDO	1.430	XV	X-ray	1.48 <sup>f</sup>
	MINDO/2	1.470	XVI	X-ray	1.47 <sup>f</sup>
VI	MINDO/3	1.457 <sup>b</sup>			

<sup>a</sup> Ref.<sup>8</sup>; <sup>b</sup> ref.<sup>9</sup>; <sup>c</sup> ref.<sup>23</sup>; <sup>d</sup> ref.<sup>20</sup>; <sup>e</sup> ref.<sup>21</sup>; <sup>f</sup> ref.<sup>22</sup>.

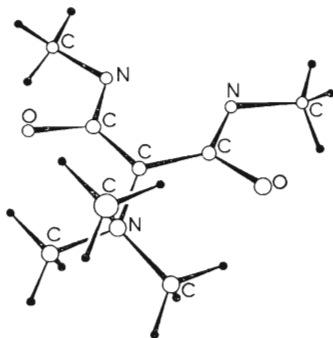


FIG. 1

Spatial Arrangement of Trimethylammonio-bis(methoxycarbonyl)methylide (VII)

The upper two nitrogen atoms in the formula should be read as oxygen atoms.

TABLE II  
Optimized Geometric Parameters of the Ylide Systems

Compound <sup>a</sup>	Bond <sup>b</sup>	r · 10 nm	Bond angle	Dihedral angle	
IV	(-) C—H	1·12	(+) (-) N CH	109·5°	(+) (-) HN CH 60°, 180°, 300°
	(-) C—H	1·12	(+) (-) N CH	109·6°	(+) (-) CN CH 60°, 180°, 300°
VII <sup>c</sup>	(-) C—C	1·415	(+) (-) N CC	118·0°	(+) (-) N CCO 0°
	C—O	1·280	(-) CCO	123·0°	(+) (-) N CCO(CH <sub>3</sub> ) 180°
	C—OCH <sub>3</sub>	1·330	(-) CCO(CH <sub>3</sub> )	122·0°	(+) (-) CN CC(O) 90°, 210°, 330°
X	(-) C—C(N)	1·405	(+) (-) N CC(N)	115·5°	(+) (-) N CCN 0°
	C≡N	1·199	(+) (-) N CC(O)	118·0°	(+) (-) N CCO 0°
			(-) CCN	179·5°	(+) (-) N CCCH <sub>3</sub> 180°
	(-) C—C(O)	1·403	(-) CCCH <sub>3</sub>	124·0°	(+) (-) CN CC(N) 0°
	C≡O	1·286	(-) CCO	126·0°	
	C—CH <sub>3</sub>	1·483			
XI	(-) C—C	1·402	(+) (-) N CC	113·6°	(+) (-) N CCN 0°
	C≡N	1·202	(-) CCN	179·0°	(+) (-) CN CC 90°, 210°, 330°

<sup>a</sup> For the geometric parameters of ylide XII see ref.<sup>23</sup>; <sup>b</sup> the C—N bond lengths are summarized in Table I; <sup>c</sup> for the compound VII standard lengths were taken: O—CH<sub>3</sub> 0·146 nm, C—H 0·109 nm.

The C—N bond, calculated by the *ab initio* method, is significantly longer than the reported standard value (0·147 nm). On the contrary, the CNDO/2 and INDO methods lead to shorter bond lengths whereas the MINDO/2, MINDO/3 and PCILO methods afford medium values, close to the experimental ones, if available.

*Geometry of the ylide carbon:* For the model, as well as for the present ammonium ylide (IV and V), all the employed semiempirical methods found a pyramidal arrangement of bonds on the ylide carbon. The same conclusion was made by the American authors<sup>8</sup> who studied the model ylide IV by the *ab initio* method; the inversion barrier was found to be 51·9 kJ mol<sup>-1</sup>. The inversion barrier calculated by us for the ylide V

amounts to  $72.7 \text{ kJ mol}^{-1}$  and  $49.6 \text{ kJ mol}^{-1}$  for the CNDO/2 and the INDO method, respectively. We found that, contrary to non-stabilized ylides, the studied stabilized ylides VII, X, XI and XII invariably have a planar arrangement on the ylide carbon. This conclusion is in accord with crystallographic studies on stabilized ylides<sup>20,24</sup>. The found out-of-plane deviation of the nitrile groups<sup>25</sup> ( $3^\circ$ ) in the pyridinium ylide XVII can be attributed to a compression in the crystal lattice.

*Bond lengths and arrangement of the anion system:* The calculated lengths of the  $\overset{(-)}{\text{C}}-\text{C}$  and  $\text{C}-\text{X}$  bonds ( $\text{X} = \text{N}, \text{O}$ ) agree with the experimental values<sup>20,25</sup> and indicate an extensive carbonium charge delocalisation. The  $\overset{(-)}{\text{C}}=\text{C}(\text{X})$  is significantly shorter than a  $\text{C}_{\text{sp}^2}-\text{C}_{\text{sp}^2}$  single bond indicating thus a partial double bond character; on the other hand, the  $\text{C}\equiv\text{N}$  and  $\text{C}\equiv\text{O}$  bonds are significantly longer. Comparison of the total energies, calculated for single conformers of the carbonyl-stabilized ylides, shows the Z,Z-conformer with a synperiplanar arrangement of the  $\overset{(+)}{\text{N}}-\overset{(-)}{\text{C}}$  and  $\text{C}-\text{O}$  bonds to be the most stable, irrespective which method was used. The energy differences between conformers are greater than  $20.0 \text{ kJ mol}^{-1}$ , guaranteeing thus conformational homogeneity of these compounds. Another situation was found by Soviet investigators<sup>26</sup> in the case of quinoline derivatives: these authors proved spectroscopically the presence of two forms to which they ascribed the structures XVIIIa and XVIIIb. This isomerism was explained by a hindered rotation.

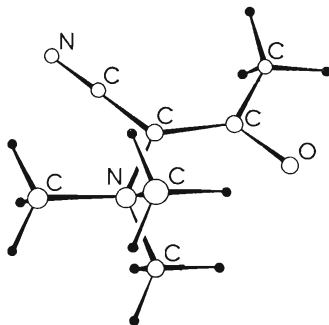
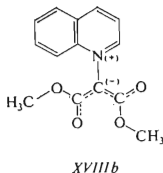
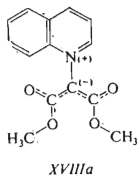
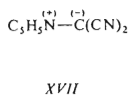
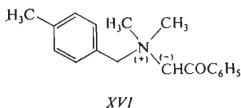
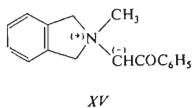
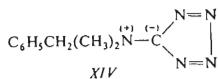
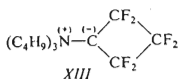
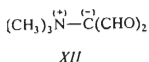
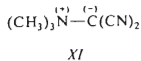
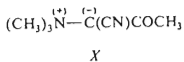
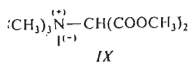
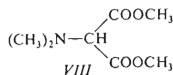
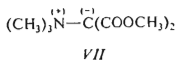
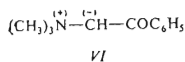
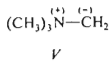


FIG 2

Spatial Arrangement of Trimethylammonioacetylcyanomethylide (X)

The full dots represent hydrogen atoms.



### Charge Distribution

The charge distribution characteristics, calculated by semiempirical methods, are summarized in Table III and IV. In the non-stabilized ylides the predominant amount of the total negative charge is concentrated at the ylide carbon which has a marked carbanion character. On the contrary, the calculated charge distribution values in stabilized ylides show a notable transfer of the negative charge to the electronegative atoms of the stabilizing groups. A comparison of the charge on the ylide carbon with the charges on the electronegative atoms is given in Table V. This finding

TABLE III  
Charge Densities,  $Q_A$ , Calculated for the Ammonium Ylides

Compound	Atom A	CNDO/2	INDO	MINDO/2
	(+)			
<i>IV</i>	N	0.125	0.227	-0.107
<i>V</i>		0.178	0.212	-0.042
<i>VII</i>		0.124		
<i>X</i>		0.141	0.177	-0.100
<i>XI</i>		0.139	0.175	-0.117
<i>XII</i>		0.143	0.183	-0.083
	(-)			
<i>IV</i>	C	-0.404	-0.431	-0.451
<i>V</i>		-0.399	-0.441	-0.403
<i>VII</i>		-0.315		
<i>X</i>		-0.215	-0.244	-0.299
<i>XI</i>		-0.212	-0.246	-0.277
<i>XII</i>		-0.207	-0.246	-0.324
<i>VII</i>	C(O, N)	0.449		
<i>X</i>		0.078	0.126	0.339
<i>X</i>		0.257	0.309	0.596
<i>XI</i>		0.079	0.127	0.351
<i>XII</i>		0.247	0.330	0.607
	(-)			
<i>VII</i>	O	-0.514		
<i>X</i>		-0.463	-0.512	-0.743
<i>XII</i>		-0.412	-0.457	-0.679
	(+)			
<i>X</i>	N	-0.257	-0.296	-0.496
<i>XI</i>		-0.272	-0.315	-0.502
<i>V, X, XI, XII</i>	H <sub>3</sub> (C)	0.007-0.049	-0.075-0.024	-0.050-0.110
<i>V, X, XI, XII</i>	C(H <sub>3</sub> )	0.065-0.071	0.111-0.138	0.095-0.182

is in accord with the work of French authors<sup>27</sup> who studied the charge distribution in nitrile-stabilized ylides by the ESCA method.

An interesting result in the study of charge distribution in the asymmetric ylide *X* is the extent of charge transfer from the ylide carbon to the stabilizing groups (CN, COCH<sub>3</sub>). From the charge densities and bond indexes calculated for the ylides *X* and *XI* we can derive the following conclusions: The charge on the nitrile nitrogen in *X* is smaller than in the symmetric derivative *XI*; the order of the C=N bond in *X* is greater, and at the same time the order of the C-C(N) bond is smaller, than in *XI*. From the charge density on the ylide carbon in *VII*, as well as from the order of the C-C(O) bond, we can derive that the ester group causes a smaller charge transfer



than formyl or acetyl groups (ylides *XI* and *XII*); this conclusion agrees with the electronic character of these groups. According to the quantum chemical calculation, a part of the positive charge is transferred from the quaternary nitrogen atom to the methyl groups.

Comparison of the gross atomic charges, obtained by the *ab initio* method, with those calculated by semiempirical methods reveals certain differences. Similarly to the semiempirical methods, the *ab initio* method shows a marked transfer of the negative charge from the ylide carbon to the electronegative atoms of the stabilizing groups (Table VI). A different charge distribution is assigned by the *ab initio* method to the trimethylammonium group. Whereas the semiempirical methods show a distribution of the positive charge among the atoms of the trimethylammonium group, the *ab initio* method on the contrary assigns the positive charge to hydrogen atoms of the methyl groups exclusively; the carbon atoms and the nitrogen atom carry the negative charge. This charge distribution does not change qualitatively when an ex-

TABLE IV  
Bond Orders,  $W_{AB}$ , Calculated for the Ammonium Ylides

Compound	Bond A—B	CNDO/2	INDO	MINDO/2
<i>IV</i>	(-) (+) C—N	0.894	0.879	0.781
<i>V</i>		0.808	0.844	0.824
<i>VII</i> <sup>a</sup>		0.875	—	—
<i>X</i>		0.802	0.820	0.796
<i>XI</i>		0.775	0.800	0.770
<i>XII</i>		0.830	0.848	0.835
<i>VII</i> <sup>a</sup>	(-) C—C(O, N)	1.212	—	—
<i>X</i>	(-) C—C(C)	1.293	1.296	1.217
<i>X</i>	(-) C—C(N)	1.189	1.183	1.058
<i>XI</i>		1.217	1.207	1.079
<i>XII</i>		1.284	1.281	1.199
<i>X</i>	C≡N	2.738	2.736	2.663
<i>XI</i>		2.699	2.705	2.636
<i>VII</i> <sup>a</sup>	C≡O	1.542	—	—
<i>X</i>		1.543	1.546	1.458
<i>XII</i>		1.665	1.669	1.545

<sup>a</sup> Because of extensiveness of the system, the calculation was carried out only by the CNDO/2 method.

TABLE V

Comparison of the Charges,  $Q_A$ , on the Ylide Carbon with the Charges on the Electronegative Atoms  $A_1, A_2$  (CNDO/2)

Compound	$Q_C^{(-)}$	$A_1$	$A_2$	$Q_{A_1}$	$Q_{A_2}$
VII	-0.315	O	O	-0.514	-0.514
X	-0.215	N	O	-0.257	-0.463
XI	-0.212	N	N	-0.272	-0.272
XII	-0.207	O	O	-0.412	-0.412

TABLE VI

The *ab initio* Calculated Gross Atomic Charges of Aliphatic Ylides

Compound	Atom A	STO - 3G	4 - 31G
IV <sup>a</sup>	$C^{(-)}$	—	-0.411
V		-0.318	-0.396
XI		-0.100	—
XII		-0.117	—
IV <sup>a</sup>	N	—	-0.861
V		-0.157	-0.768
XI		-0.151	—
XII		-0.155	—
IV <sup>a</sup>	H <sub>CH<sub>2</sub></sub>	—	0.048
V		-0.067	0.049
IV <sup>a</sup>	H <sub>NH<sub>3</sub></sub>	—	0.373-0.40
V	H <sub>CH<sub>3</sub></sub>	0.072-0.101	0.146-0.216
XI		0.082-0.113	—
XII		0.075-0.115	—
V	C <sub>CH<sub>3</sub></sub>	-(0.065-0.078)	-(0.200-0.206)
XI		-(0.073-0.075)	—
XII		-(0.071-0.089)	—
XI	C(O, N)	0.020	—
XII		0.093	—
XI	$N^{(-)}$	-0.259	—
XII	$O^{(-)}$	-0.346	—

<sup>a</sup> Net atomic charges, ref.<sup>8</sup>.

TABLE VII  
Calculated and Measured Dipole Moments of Ammonium Ylides

Compound	$\mu_{\text{calc}}, \text{Cm } 10^{-30}$				$\mu_{\text{exp}} 10^{-30}$
	CNDO/2	INDO	MINDO/2	<i>ab initio</i> <sup>a</sup>	
VI	14.40	14.65	—	—	<sup>b</sup>
X	21.75	22.04	19.38	—	20.7
XI	30.51	31.69	34.93	29.35	27.2
XII <sup>c</sup>	16.29	16.97	10.98	16.95	16.2

<sup>a</sup> Basis STO-3G; <sup>b</sup> value for the sulfonium analogue:  $14.4 \text{ Cm } 10^{-30}$  (the ammonium and sulfonium analogues have very similar dipole moments<sup>28</sup>); <sup>c</sup> ref.<sup>23</sup>.

tended basis is used (4–31G). The same results were obtained by American authors<sup>8</sup> studying charge distribution in the ylide IV.

Table VII lists dipole moments of the optimal conformations together with the experimental values. As seen, the best accord is obtained with the values calculated by the CNDO/2, INDO and *ab initio* methods. For extremely polar systems the calculated dipole moment is somewhat higher. However, on the whole, the calculated dipole moments agree well with the experimental value and confirm the proposed geometric arrangements.

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