TRIMETHYLAMMONIODIFORMYLMETHYLIDE: STRUCTURE AND CHARGE DISTRIBUTION

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Geometric arrangement of trimethylammoniodiformylmethylide (*I*) and charge distribution in this compound were calculated by quantum chemical methods (EHT, CNDO/2, INDO, PCILO, MINDO/2, *ab initio*). Total energy minimum was found for the arrangement *If*. The experimentally found dipole moment agrees very well with that calculated for this conformation.

The aim of our recent study was to determine the geometric arrangement of the recently synthesised trimethylammoniodiformylmethylide (*I*) and to compare the calculated charge distribution with the experimentally found reactivity[1]. Compound *I* belongs to the most stable ammonium ylides known. However, quantum chemical study of this type of compounds has been hitherto limited only to model systems[2-4] and to non-stabilized ylides, for which the calculated characteristics cannot be compared directly with the experimental data.

The ylide *I* can be regarded upon as a malonaldehyde derivative. The structure of malonaldehyde derivatives was found to depend on the kind of substituent and in some cases also on the medium. For the unsubstituted malonaldehyde, CNDO/2 (ref.[5]) as well as *ab initio*[6] calculations have led to a structure containing an intramolecular hydrogen bond. However, as shown by NMR spectra[7], the conformation of this compound depends on the medium. Depending on the substituent, substituted malonaldehydes were found (X-ray, NMR, IR) to exist in structures with intramolecular hydrogen bond[8-10] or in the "all *trans*" conformation[11-15] (with intermolecular hydrogen bond). Recently, structure of two carbonyl-stabilized ammonium ylides *II* and *III* has been determined by X-ray analysis[16]. In both cases a synperiplanar arrangement of the $\overset{(+)}{\text{N}}\text{—}\overset{(-)}{\text{C}}$ and C—O bonds has been found, indicating thus a planar arrangement at the ylide carbon atom.

Conformational homogeneity problems concerning a series of carbonyl-substituted phosphonium and sulfonium ylides were studied spectroscopically by Soviet authors[17]. Spectra of these compounds exhibit a series of strong bands in the region 1720–1600 cm^{-1}, assigned to conformational non-homogeneity of the studied systems. It was found that in a medium of low dielectric constant, phosphonium,

sulfonium and arsonium dicarbonyl-stabilized ylides exist almost exclusively as the Z,Z-conformers[17-19]; the same was observed for the crystalline lattice. Low-temperature NMR spectra of alkoxycarbonyl-stabilized phosphonium[20,21] and sulfonium ylides[22] indicate the existence of two rotamers.

The stability of methylides, containing electronegative groups, is explained by delocalisation of the electron density from the ylide carbon to the stabilizing groups. The low C—O stretching vibration values[23-26], as well as the X-ray data, are in accord with this concept; the $\overset{(-)}{C}$—C(O) bonds in the carbonyl-stabilized ylides[16,27] are significantly shorter than the standard C—C(O) bond; on the contrary, the C—O bond was found to be significantly longer. The problem of charge distribution in stabilized ylides has not been hitherto quantum chemically investigated; for the ylide I this problem is solved in the present paper.

CALCULATIONS

The EHT (ref.[28]) calculations were carried out on an IBM 370 computer using the standard program. The CNDO/2 (ref.[29,30]), CNDO/S (ref.[31,32]), INDO (ref.[33]), and MINDO/2 (ref.[34]) calculations were performed using the standard parameterisation. The *ab initio* calculations were performed using the Gaussian 70 program[35] with the STO-3G basis[36]. For the PCILO (ref.[37]) calculations the bond polarities were optimized in each step. In the configurational interaction (CNDO/SCI), 25 monoexcited configurations were considered and 5 highest occupied and 5 lowest unoccupied MO were taken. The bicentric repulsion integrals were approximated according to Mataga and Nishimoto[38]. The charge distribution was studied by EHT, CNDO/2, INDO, MINDO/2 and *ab initio* methods; the same methods were used in dipole moment calculations.

For the automatic optimization of the malonaldehyde anion geometry we employed the Derival program[39] and the calculations were performed on an IBM 370 computer. The geometric optimization of the ylide *I* was carried out by the CNDO/2 method under assumption of tetrahedral arrangement of the trimethylammonium group for which standard bond lengths and bond angles[40] were taken ($r_{(C-N)} = 0{\cdot}147$ nm, $r_{(C-H)} = 0{\cdot}109$ nm, $\sphericalangle$ NCH = 109·47°). For the molecule part, representing the malonaldehyde grouping, we performed a complete optimization.

RESULTS AND DISCUSSION

Geometric arrangement of I. Considering the existing knowledge of malonaldehyde derivatives structure, we based our determination of the ylide geometry on the six forms *Ia*–*If*. We found that the forms *Ia*, *Ic* and *Ie* with localised bonds are by about 50 kJ mol^{-1} energetically less stable than the corresponding forms *Ib*, *Id* and *If* and therefore only the latter three were considered further. The optimized geometric parameters obtained by the CNDO/2 method are given in Table I, together with the known data about the geometry of nitrogen ylides. Table II lists the total energy content of the particular conformers in their optimized geometry.

Three methods (CNDO/2, INDO and PCILO) prefer the structure *If* whereas the EHT method prefers the conformer *Ib*. Due to neglecting the electron repulsion,

TABLE I

Optimized Bond Lengths and Bond Angles in the Ylide *I*, Compared with Known Data

Bond	Bond length, nm[a]	Bond angle	
$\overset{(-)(+)}{C—N}$	0·145(0·146[b], 0·147[c], 0·148[c])	$\overset{(+)(-)}{N\ CC(O)}$[d]	120·8°
$\overset{(-)}{C—C(O)}$	0·1402(0·1417[b], 0·136[c], 0·134[c])	$\overset{(-)}{CC(O)O}$[d]	127·7°
C—O	0·1283(0·1234[b], 0·127[c], 0·130[c])	$\overset{(-)}{CC(O)H}$[d]	119·5°
C(O)—H	0·12		

[a] The known data are given in parentheses; [b] the value calculated by MINDO/3 method for trimethylammoniobenzoylmethylide[41]; [c] the values determined by X-ray analysis of *II* and *III* (ref.[16]); [d] dihedral angles in the malonaldehyde part are 0° and 180°.

TABLE II

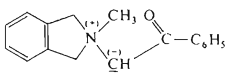
Calculated Total Energy, $-E_{Tot}$ (eV), for Conformers of the Ylide *I*

Conformer	EHT[a]	CNDO/2	INDO	MINDO/2	PCILO
Ib	959·92	2 705·35	2 604·77	1 768·28	2 713·78
Id	959·88	2 705·69	2 605·15	1 768·35	2 713·95
If	959·85	2 705·94	2 605·42	1 768·08	2 714·33

[a] Electron energy.

the EHT method is not able to recognize the disadvantage of this geometric arrangement which involves a short distance between the negatively charged oxygen atoms. The MINDO/2 method shows the structure *Id* to be the most advantageous; this is not surprising since this method strongly overestimates non-bonding interactions, particularly in the case of hydrogen atoms.

The conformation *If* is fixed by attraction between the negative oxygen atoms and the trimethylammonium group. This conformation is also the best concerning the negative charge transfer from the ylide carbon to the oxygen atoms. The conformer *If* corresponds to an optimum arrangement of the malonaldehyde anion (Derival-INDO). The planar arrangement on the ylide carbon, found to be the best in terms of energy, is in accord with the X-ray data[16] (*II* and *III*) and with the concept of sp^2 hybridisation of the ylide carbon in stabilized ylides.



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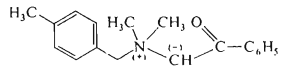

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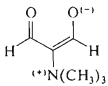
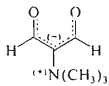


Ia



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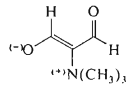

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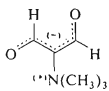
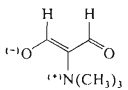
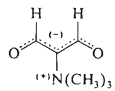


Id



Ie



If

In accord with the ^{1}H-NMR spectrum of *I* which displays methyl protons as a single signal, indicating thus a free rotation around the $\overset{(-)}{C}—\overset{(+)}{N}$ bond, CNDO/2 calculation has found a low barrier to rotation amounting to 1·66 kJ mol^{-1}. This barrier corresponds to the arrangement in which the methyl carbon atom is situated in the plane of the malonaldehyde part. The optimum arrangement of the trimethylammonium group is depicted in Fig. 1.

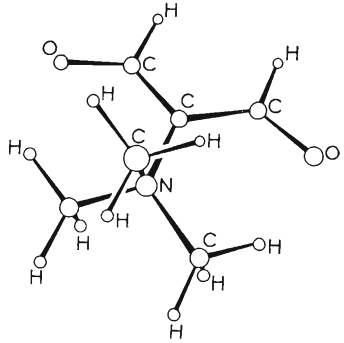


FIG. 1

Spatial Arrangement of Trimethylammoniodiformylmethylide (*I*)

Since the carbonyl-stabilized ylides have been shown to be conformationally non-homogeneous[17], it was necessary to determine the energy difference between the conformers *Id* and *If* and the height of the barrier between them. If we assume a low transition barrier, the energy differences, calculated on the basis of the Boltzman distribution, guarantee conformational homogeneity of the ylide *I* (Table III). Moreover, the barrier to rotation around the $\overset{(-)}{C}$—C(O) bond (geometry optimized for the perpendicular arrangement of the formyl groups planes) was calculated to be 102·29 kJ mol^{-1} (CNDO/2) and 106·86 kJ mol^{-1} (INDO). We can thus infer that the compound *I* is conformationally homogeneous and exists in the conformer *If*.

Also a comparison of the observed dipole moment with the values calculated for structures *Ib*, *Id* and *If* (Table IV) speaks unequivocally for the form *If*. A particularly good agreement was found with semiempirical methods considered to be most reliable for dipole moment calculations (CNDO/2, INDO) (ref.[43]); also the accord with the *ab initio* calculations was very good.

TABLE III

Energy Differences, ΔE_{Tot} (kJ . mol^{-1}), between Conformers of the Ylide *I*

Conformer	EHT[a]	CNDO/2	INDO	MINDO/2	PCILO
Ib—*If*	−6·7	57·0	63·2	−19·5	53·2
Ib—*Id*	−3·3	33·7	37·1	6·9	16·3
Id—*If*	−3·4	23·3	26·0	−26·5	36·9

[a] Electron energy.

TABLE IV

Dipole Moments, μ_{calc} (Cm . 10^{-30}), Calculated for Conformers of the Ylide *I* (reported[42] experimental value μ_{exp} = 16·2)

Conformer	EHT	MINDO/2	INDO	CNDO/DEL BENE	CNDO/2	*ab initio*
Ib	91·18	49·28	45·11	—	45·89	—
Id	57·20	32·26	32·24	35·07	32·36	—
If	14·21	10·98	16·97	15·83	16·29	16·95

Electronic Structure of the Ylide I

The calculated charge distribution characteristics (charge density Q_A (ref.[44]) and Wiberg bond index W_{AB} (ref.[45])) are summarized in Tables V – VIII. The EHT method is not very suitable for the comparison because it overestimates the atomic charge localisation and affords thus a too high charge distribution[46]; it seems that it does not reflect at all the physical reality of the charge distribution since it assigns a positive charge to the ylide carbon atom. It follows from comparison of the calculated characteristics of the single conformers (Table VI) that the negative charge on the ylide carbon atom decreases with the decreasing energy content of the conformer (*Ib* → *If*) whereas the negative charge on the oxygen atoms increases in the same direction.

The charge drop on the ylide carbon agrees with the experimentally found reactivity; the nucleophilicity is markedly lower than that of the non-stabilized and monocarbonyl-stabilized ammonium ylides[47]. In the conformation *If*, the negative charge transfer from the ylide carbon to the oxygen atoms of the formyl groups is facilitated to the greatest extent. The same conclusion followed from the confrontation of bond indexes of the single conformers (Table VII). With decreasing total energy of the system the order of the $\overset{(-)}{C}$—C(O) bond increases whereas that of the C—O bond decreases. As shown by all the methods employed, the $\overset{(-)}{C}$—$\overset{(+)}{N}$ bond stability increases with decreasing energy of the system. Although its bond index is the lowest of all the bonds

TABLE V

Charge Densities, Q_A (in atomic units), in the Conformer *If*

Atom A	EHT	CNDO/2	INDO	MINDO/2	*ab initio*[a]
H_{CHO}	0·082	−0·050	−0·080	−0·050	0·034
H_{CH_3}	0·120–0·150	0·005–0·035	−0·010–0·006	−0·050–0·110	0·075–0·115
$\overset{(-)}{C}$	0·173	−0·207	−0·246	−0·324	−0·117
C(O)	0·690	0·247	0·330	0·095	0·083
$\overset{(+)}{C}(N)^b$	−0·191	0·051	0·111	0·095	−0·089
$\overset{(+)}{N}$	0·129	0·143	0·183	−0·083	−0·155
O	−1·249	−0·412	−0·457	−0·679	−0·346

[a] STO-3G basis, gross atomic charges; [b] for the methyl carbon with dihedral angle $\theta(\overset{(-)}{C}(O), C, \overset{(+)}{N}, C) = 30°$.

TABLE VI

Comparison of Charge Densities, Q_A (in atomic units), of the Ylide Carbon and Oxygen in the Formyl Group of the Conformers of *I*

Conformer	Atom	CNDO/2	INDO	MINDO/2
Ib		−0·215	−0·255	−0·371
Id	$\overset{(-)}{C}$	−0·211	−0·251	−0·344
If		−0·207	−0·246	−0·324
Ib		−0·354	−0·398	−0·599
Id	$\overset{(-)}{O}$	−0·371	−0·415	−0·653
If		−0·412	−0·458	−0·679

TABLE VII

Bond Indexes (W_{AB}) of Conformer *If*

Bond A—B	CNDO/2	INDO	MINDO/2
C(O)—H	0·933	0·915	0·934
$\overset{(-)}{C}$—C(O)	1·284	1·281	1·200
$\overset{(-)\,(+)}{C}$—N	0·830	0·848	0·835
C═O	1·665	1·670	1·545
$\overset{(+)}{C}$—N[a]	0·954	0·957	0·906

[a] Methyl carbon with dihedral angle $\theta(C(O), \overset{(-)\,(+)}{C}, N, C) = 30°$

in the molecule (Table VIII), according to the experimental evidence the fission of this bond is very difficult. The semiempirical methods (excluding EHT) as well as the *ab initio* method, agree in description of the charge distribution in the malonaldehyde part. On the other hand, these methods describe differently the charge distribution in the trimethylammonium group. The semiempirical methods afford an equal distribution of the positive charge whereas the *ab initio* method concentrates the charge to the hydrogen atoms of this group. A more detailed comparison of the

TABLE VIII
Comparison of Bond Indexes, W_{AB}, for Conformations of the Ylide *I*

Conformer	Bond	CNDO/2	INDO	MINDO/2
Ib		1·268	1·265	1·144
Id	$\overset{(-)}{C}{=}C(O)$	1·273	1·271	1·167
If		1·284	1·281	1·200
Ib		1·701	1·708	1·648
Id	C=O	1·692	1·699	1·603
If		1·665	1·669	1·545
Ib		0·814	0·835	0·779
Id	$\overset{(-)(+)}{C}{-}N$	0·822	0·841	0·806
If		0·830	0·848	0·835

charge distribution in a series of ammonium ylides, together with the nature of the $\overset{(-)\,(+)}{C{-}N}$ bond, is given in ref.[42].

We can summarize that of the semiempirical methods the most suitable for the quantum chemical treatment of dipolar ylide compounds are the CNDO/2, INDO and PCILO methods; also the *ab initio* method serves well for the description of these systems.

Calculation of the Electronic Spectrum

The measured UV spectrum of the ylide *I* exhibits a single symmetrical band of high extinction[1]. The calculated spectrum displayed in the measured region only one transition due to the HOMO-LUMO transition of the $\pi \rightarrow \pi^*$ type. The calculated and found values are summarized in Table IX. Since the compound I is highly polar, it was not possible to measure its UV spectrum in a nonpolar solvent. As shown by data for $(CH_3)_2C_{12}H_{25}\overset{(+)\ (-)}{N{-}C}(CHO)_2$ (*IV*), the position of UV bands of such compounds is solvent-independent. The agreement between calculation and experiment was not improved even by variation of the constant $\varkappa$.

Addition Compounds of the Ylide I *with Hydrogen Halides and Inorganic Salts*

As found previously[1,48], the ylides containing a malonaldehyde grouping form adducts *a*) with hydrogen halides and *b*) with inorganic salts.

TABLE IX
Comparison of Calculated and Measured UV Spectra of the Ylides *I* and *IV*

Method	λ_{max}, nm (ε 10^{-3})	*f*
CNDO/S	243·1	0·8177
exp *I* (H_2O)	257 (28·8)	0·4623
($C_2H_5O_4$)	257 (28·6)	—
IV ($C_2H_5O_4$)	257 (28·5)	—
(C_6H_{12})	255 (20·7)	—

a) As the simplest model for the quantum chemical treatment we chose the adduct of the ylide *I* with hydrogen fluoride (*V*, hitherto unknown). The arrangement with the calculated minimum energy is depicted in Fig. 2. It is obvious that, according to the quantum chemical calculation, the presence of a hydrogen halide forces the malonaldehyde part of the molecule to assume a cyclic structure.

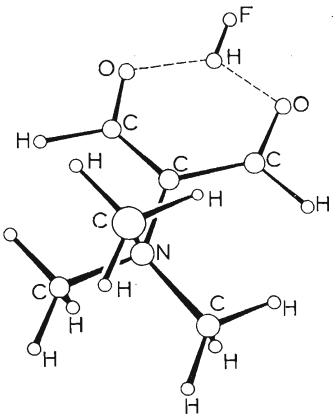


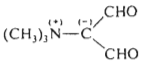
FIG. 2
Spatial Arrangement of the Adduct of Ylide *I* with Hydrogen Fluoride (for geometric parameters see ref.[47])

b) The adducts of ylides with inorganic salts have been hitherto studied mostly on series of phosphorus derivatives. Phosphonium ylides form stable associates with many lithium salts which have been shown by analytical data to be equimolecular complexes[49]. It is assumed that the ylide carbon forms a contact ion pair or a solvated ion pair with the lithium cation[50]. For the adduct $\overset{(+)}{X}—\overset{(-)}{C}R_2.MY$ (X = P, N, S) following geometric arrangements can be suggested:

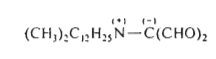
A

B

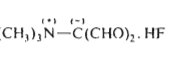
C



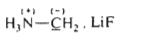
I



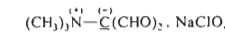
IV



V



VI



VII

The formation of ylide adducts with inorganic salts is not restricted only to non-stabilized ylides; as we already described[1], the ylide *I* forms analogous adducts. Since this problem has not been studied as yet, we wanted to determine fundamental geometric features of adducts of this type. As a model we chose $\overset{(+)}{H_3N}—\overset{(-)}{C}H_2.LiF$ (*VI*). According to the automatic optimization method (DERIVAL, INDO), the

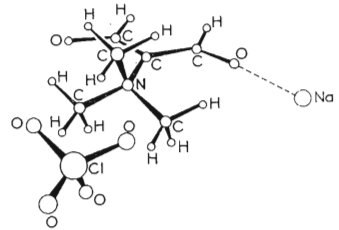


FIG. 3

Spatial Arrangement of the Adduct of Ylide *I* with Sodium Perchlorate (for geometric parameters see ref.[47])

lithium atom interacts with the electron pair of the ylide carbon whereas the fluoride anion interacts electrostatically with hydrogen atoms of the ammonium group (nearest to the structure *C*). Investigation of many possible arrangements of the adduct of the ylide *I* with sodium perchlorate (*VII*) (CNDO/2) led to the structure depicted in Fig. 3. Contrary to the case of adducts with hydrogen halides, we did not find the cyclic arrangement to be the optimum form, probably as a result of the sodium atom size.

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