STRUCTURAL INVESTIGATIONS OF SUBSTITUTED METHYLENE-MALONALDEHYDES BY X-RAY CRYSTALLOGRAPHY AND NMR SPECTROSCOPY

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Crystal and molecular structure of three substituted methylenemalonaldehydes *I—III* was studied. The spatial arrangement of the monosubstituted derivative *I* differs significantly from that of the disubstituted methylenemalonaldehydes *II* and *III*, not only in the solid state conformation of the malonaldehyde fragment but also in the length of the ethylenic C=C double bond and in its distorsion. The structures found in crystal are compared with conformations in solutions determined by NMR spectroscopy.

Molecules of distorted geometry are of great interest to organic chemists[1,2]. Among sterically crowded organic molecules we can count also tetrasubstituted ethylenes. In many respects, these compounds have very interesting properties and behave analogously[3]. Studies on crowded ethylenes have been aimed at their electronic spectra[4,5] and dynamic stereochemical behaviour[6,7] (*e.g.* barriers to rotation in α,β-substituted styrenes[8] and stilbene derivatives[9]). Also thermochemical[10] and chiroptical[11] properties of these systems have been studied. Recently, elongation and twist of the C=C double bond in tetrasubstituted ethylenes attract attention[3,12,13] in connection with attempts to prepare the hitherto undescribed tetra-tert--butylethylene.

In connection with preparation and synthetic utilization of methylenemalonaldehydes[14−16] we investigated the structure of mono- and disubstituted derivatives of these compounds. Disubstituted (diaryl or heteroaryl) methylenemalonaldehydes are attractive substrates because of significant steric crowding around the C=C double bond. This aspect has been followed by us by comparison of reactivity of mono- and disubstituted methylene malonaldehydes[17] and by ^{1}H and ^{13}C NMR spectroscopic studies on conformation in solution[18,19]. The aim of the present communication is to determine the crystal and molecular structure of mono- and

diarylmethylenemalonaldehydes and to compare it with the conformation in solution as well as with the optimized geometry obtained by quantum chemical methods.

EXPERIMENTAL

Compounds *I—IV* were prepared according to the described procedures[14–16]. The electronic absorption spectra were recorded on a Specord UV-VIS (Zeiss, Jena) instrument in n-hexane and dichloromethane (c 1—5 . 10^{-5} mol 1^{-1}). The ^{1}H and ^{13}C NMR spectra were measured on Varian XL-200 and Jeol FX-60 spectrometers. Quantum chemical calculations were performed using the methods CNDO/2 and INDO with original parameterization[20] in the sp basis, and the *ab initio* method in the STO-3G basis[21] (Gaussian 70 computer program[22]). The total optimization was done using the MNDO method[23].

X-ray crystallography: Data for *I—III* were collected at ambient temperature on a Nicolet R3m diffractometer. Mo K_α radiation ($\lambda = 0.71069$ Å)* with graphite monochromator was used. Accurate cell parameters were obtained for *I, II* and *III* from 10, 22 and 10 centered reflections

TABLE I

Crystallographic data

Compound	*I*	*II*	*III*
Formula	$C_8H_6O_2S$	$C_{16}H_{12}O_2$	$C_{14}H_{10}O_2S$
Space group	*Pbca* (61)	$P2_1/c$ (14)	$C2/c$ (15)
a, Å	7·274(0·005)	9·674(0·002)	16·67(0·02)
b, Å	11·430(0·008)	16·565(0·006)	9·31(0·01)
c, Å	18·285(0·009)	7·684(0·003)	15·88(0·02)
B, deg.	—	90·61(0·03)	107·8(0·1)
V, Å^3	1 520(2)	1 231·4(0·7)	2 347(5)
Z	8	4	8
μ(Mo K_α), cm^{-1}	0·85	0·85	0·85
Scan range	5·0—50·0	4·0—50·0	0·0—100·0
hkl range	0, 0, 0—9, 14, 22	0, 0, −12—10, 20, 12	0, 0, 0—10, 10, 10
Scan mode	V/2θ	$\omega/2\theta$	$\omega/2\theta$
No. of reflections	1 576	2 425	2 280
Measured No. of unique data^a	898	1 634	1 296
$R_1{}^b$	0·0367	0·0416	0·0560
$R_2{}^c$	0·0367	0·0416	0·0655
Goodness of the fit	0·819	0·574	1·055

^{a} $|F| > 5\delta(|F|)$; ^{b} $R_1 = \dfrac{\sum ||F_0| - |F_c||}{\sum |F_0|}$; ^{c} weight $= 1/(\delta^2(F) + 0.0005F^2)$.

* 1 Å $= 10^{-10}$ m.

and are listed, along with other crystallographic data, in Table I. Intensities were corrected for background, polarisation and Lorenz factors. Data collection was conducted according et standard procedures; data relevant to this phase of the work are also presented in Table I. Spaco groups 61, 14 and 15 were assigned to *I*, *II* and *III* uniquely with systematic absences. The structures were solved by direct methods. All nonhydrogen atoms were found in direct method solu-

TABLE II

Atomic coordinates ($.10^4$) for compounds *I*—*III*

Atom	x	y	z
	2-Thienylmethylenemalonaldehyde (*I*)		
S	1 895(1)	9 534(1)	1 935(1)
O(1)	1 973(3)	9 040(2)	3 393(1)
O(2)	982(4)	11 678(2)	4 797(1)
C(1)	1 638(5)	9 842(3)	3 793(2)
C(2)	793(5)	11 856(3)	4 157(2)
C(3)	1 132(4)	11 018(3)	3 569(2)
C(4)	920(4)	11 401(3)	2 879(2)
C(5)	1 151(4)	10 920(3)	2 168(2)
C(6)	836(5)	11 556(3)	1 533(2)
C(7)	1 188(5)	10 948(4)	895(2)
C(8)	1 778(5)	9 856(3)	1 031(2)
	Diphenylmethylenemalonaldehyde (*II*)		
O(1)	2 354(2)	3 763(1)	3 066(3)
O(2)	4 771(2)	2 834(1)	3 664(3)
C(1)	1 964(2)	3 131(1)	2 466(3)
C(2)	3 920(2)	2 311(2)	3 780(3)
C(3)	2 526(2)	2 331(1)	2 966(3)
C(2)	3 920(2)	2 311(2)	3 780(3)
C(4)	1 801(2)	1 637(1)	2 725(2)
C(5)	322(2)	1 623(1)	2 234(3)
C(6)	− 622(2)	2 167(1)	2 922(3)
C(7)	−2 000(2)	2 145(2)	2 432(3)
C(8)	−2 453(2)	1 576(2)	1 242(3)
C(9)	− 1 540(2)	1 023(2)	569(3)
C(10)	− 162(2)	1 043(1)	1 060(3)
C(11)	2 470(2)	840(1)	2 971(3)
C(12)	1 859(3)	267(2)	4 038(3)
C(13)	2 476(3)	−472(2)	4 317(4)
C(14)	3 705(3)	−653(2)	3 518(4)
C(15)	4 317(3)	− 100(2)	2 440(4)
C(16)	3 710(2)	649(2)	2 160(3)

TABLE II

(*Continued*)

Atom	x	y	z
		Phenyl-2-thienylmethylenemalonaldehyde (*III*)	
S	4 800(1)	774(1)	8 863(1)
O(1)	1 911(2)	−494(4)	9 937(2)
O(2)	1 503(2)	−2 758(4)	8 701(3)
C(1)	2 554(3)	−477(5)	9 730(3)
C(2)	2 039(3)	−2 207(5)	8 449(3)
C(3)	2 647(2)	−1 122(4)	8 927(3)
C(4)	3 303(2)	−732(4)	8 614(2)
C(5)	3 768(2)	593(4)	8 869(2)
C(6)	3 490(3)	1 881(5)	9 145(3)
C(7)	4 134(4)	2 934(6)	9 361(3)
C(8)	4 861(3)	2 466(5)	9 252(3)
C(9)	3 560(2)	−1 720(4)	8 008(3)
C(10)	3 705(3)	−1 221(5)	7 227(3)
C(11)	3 916(3)	−2 184(6)	6 862(3)
C(12)	4 001(3)	−3 605(6)	6 881(3)
C(13)	3 884(3)	−4 111(4)	7 646(3)
C(14)	3 652(3)	−3 198(5)	8 193(3)

tions and hydrogens from successive Fourier maps. SHELXTL program package on a NOVA 3 minicomputer was used in all calculations. Anisotropic refinements for the nonhydrogen atoms and isotropic refinements for hydrogens converge at $R = 0.0416, 0.0367, 0.0560$ and $R = 0.0416$, 0.0367, 0.06550 for *I*, *II* and *III*, respectively. The atomic coordinates are given in Table II. Listing of observed and calculated structure factors, thermal parameters and hydrogen positional parameters is available on request (T.A.P.).

RESULTS AND DISCUSSION

The results of the X-ray measurements on compounds *I−III* are summarized in Table II. They served for calculation of parameters describing planarity of the molecule, rotation of the aryl and formyl groups and, last but not least, length and twist of the C=C double bond.

Whereas the monosubstituted compound, 2-thienylmethylenemalonaldehyde (*I*), has been found to be almost planar with only very small out-of-plane deviations (Table III), in the disubstituted (diaryl, heteroaryl) methylenemalonaldehydes the spatial arrangement is markedly influenced by steric interactions. The X-ray data show that in the disubstituted derivatives the steric interactions are relieved in three

ways: *a*) by deviation of the aryl from the methylenemalonaldehyde plane, *b*) by rotation of the formyl groups, and *c*) by twist of the C=C olefinic double bond and its elongation. The ways *a*) and *b*) reduce the conjugation energy. The found bond lengths and bond and torsion angles in compounds *I−III* are compared in Tables III−V.

As seen from Table IV, bond lengths of the C=C double bonds in the mono- and disubstituted methylenemalonaldehydes differ significantly. In 2-thienyl-methylenemalonaldehyde (*I*) the C=C bond length is similar to that in unsubstituted

TABLE III

Comparison of out-of-plane deviations in compounds *I−III*

Kind of deviation	*I*	*II*	*III*
Distorsion of carbonyls[a]			
C(1)—O(1)	0·4	17·8	15·6
C(2)—O(2)	2·6	16·2	9·1
Twist C=C			
C(3)—C(4)	2·4	10·9	20·1
Rotation of aryl	1·0	51·2	45·8[b]
(heteroaryl)		38·9	26·6[c]

[a] Carbonyl torsion angles from the plane through atoms C(1)—C(2)—C(3)—C(4); [b] for benzene nucleus; [c] for thiophene nucleus.

TABLE IV

Comparison of bond distances (Å) in the equivalent part of molecules *I, II,* and *III* based on X-ray results

Bonded atoms	*I*	*II*	*III*
C(1)—O(1)	1·198(4)	1·203(4)	1·214(7)
C(2)—O(2)	1·196(4)	1·200(3)	1·201(7)
C(1)—C(3)	1·453(5)	1·481(3)	1·460(7)
C(2)—C(3)	1·460(5)	1·480(3)	1·467(6)
C(3)—C(4)	1·345(4)	1·358(3)	1·380(6)
C(4)—C(5)	1·421(4)	1·477(3)	1·448(5)
C(5)—S	1·727(3)	—	1·732(4)
C(4)—C(11)	—	1·482(3)	—
C(4)—C(9)	—	—	1·486(6)

ethylene (134 pm) whereas in diphenylmethylenemalonaldehyde (II) and phenyl-2- -thienylmethylenemalonaldehyde (III) the C=C bond is longer as the result of steric repulsion (Table IV, Fig. 1 – 3). The completely preserved (undisturbed by non-planarity) conjugation in I (Table III) is confirmed also by the =C—CHO bond lengths (145·3 pm), which are markedly shorter than those in the derivative II (148·1 pm) (Table IV).

Concerning the bond angles (Table V, Fig. 1 – 3), very interesting values have been found for the monosubstituted derivative I: the asymmetry of the malonal-dehyde fragment (the difference between the angles C(3)—C(2)—O(2) and C(3)— —C(1)—O(1) amounts to 9°. The most notable, however, is the angle C(3)—C(4)— —C(5) whose value is 136° (Table V). This marked bond angle deformation allows the molecule to attain planarity and thus gain the conjugation energy. This angle is 13·4° larger than the corresponding angle in the disubstituted derivative III. In Table III we find angles of deviation of aryl group from the malonaldehyde grouping plane, carbonyl torsion angles and angles of the olefinic double bond twist in com-
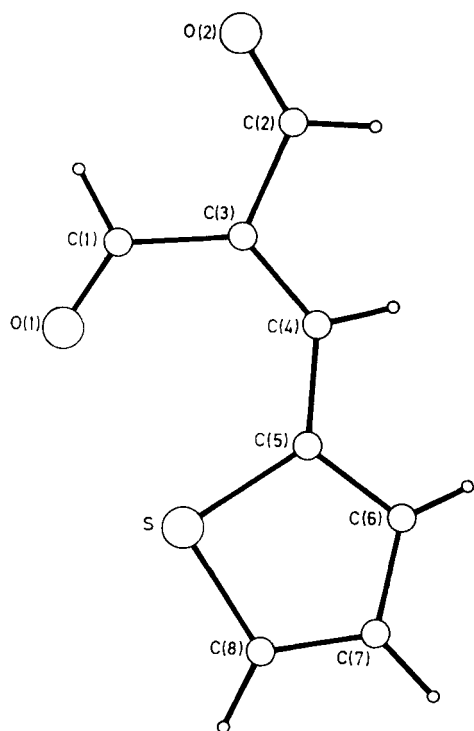
FIG. 1

Spatial arrangement found for compound I
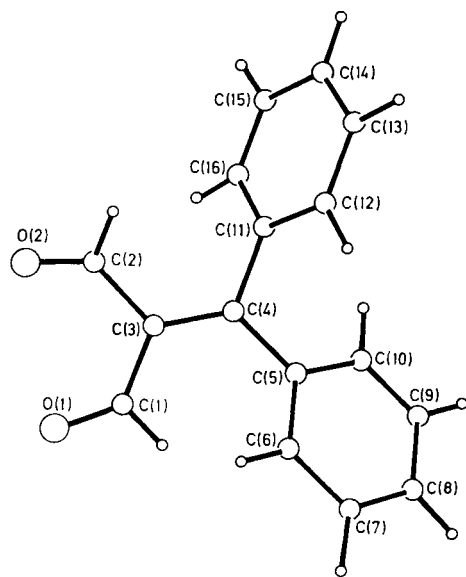
FIG. 2

Spatial arrangement found for compound II

pounds $I-III$. As already mentioned, the monosubstituted derivative I is almost planar. For the disubstituted derivatives II and III we have found significant out-of--plane deviations for all the parameters mentioned. The observed torsion angles for the phenyl rings in compound II and for the phenyl and thiophene rings in compound III mean a significant deviation from the methylenemalonaldehyde plane forced by the steric repulsion between the aromatic nucleus and the C and H atoms of the formyl group. The difference of 12° between the torsion angles of the benzene rings

TABLE V

Comparison of bond angles in the equivalent parts of molecules I, II, and III based on X-ray results

| Bonded atoms	I	II	III
O(1)—C(1)—C(3)	126·0(3)	124·5(2)	124·8(4)
O(2)—C(2)—C(3)	126·1(3)	125·1(2)	126·1(5)
C(1)—C(3)—C(2)	116·2(3)	117·4(2)	119·6(4)
C(1)—C(3)—C(4)	126·5(3)	122·3(2)	120·9(4)
C(2)—C(3)—C(4)	117·3(3)	120·3(2)	119·5(4)
C(3)—C(4)—C(5)	136·0(3)	123·1(2)	122·6(4)
C(3)—C(4)—C(11)	—	120·3(2)	—
C(3)—C(4)—C(9)	—	—	119·2(3)
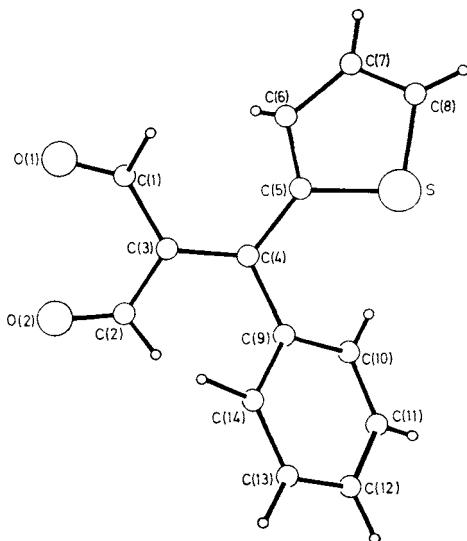
FIG. 3
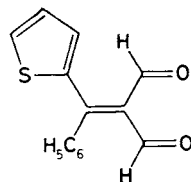
Spatial arrangement found for compound III

in *II* (Table III) can be ascribed to different interactions of the phenyl groups with the neighbouring molecules in the unit cell. Substitution-dependent deviation of aryl groups from planarity was observed also in solution by NMR spectroscopy[19].
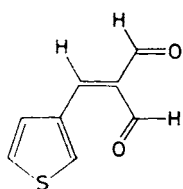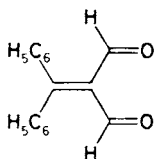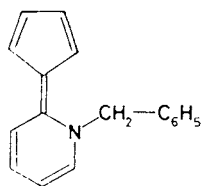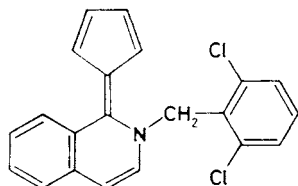
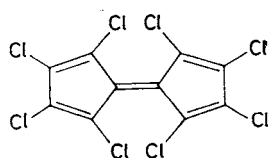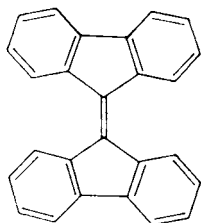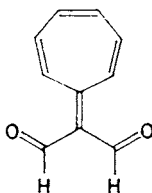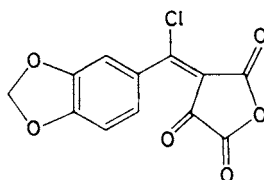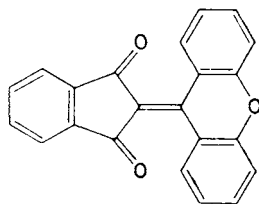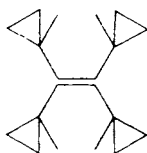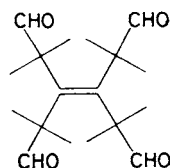The steric crowding is alleviated also by rotation about the =C—CHO bond which brings the formyl oxygen and hydrogen atoms above and below the methylenemalonaldehyde plane: in compound *II* this torsion is about 17°, in compound *III* the torsion angles of the two formyl groups differ quite substantially, higher torsion being found for the CHO group Z-relative to the thiophene ring. The bond length of the C=C double bond and its twist (Tables III and IV) rank the disubstituted methylenemalonaldehydes among the sterically crowded ethylenes. Figures 2 and 3 represent one of the possible spatial arrangements of *II* and *III*, respectively, corresponding to absolute values of the C=C bond twist given in Table III. Sterically crowded olefins often contain nonplanar C=C double bonds[24,25] (Table VI).

It has been found that the barrier to rotation about the C=C bond is lower in ethylenes containing a strong donor on one olefinic carbon atom and a strong acceptor on the other as the result of stabilization of the zwitterion transition state[26]. Combination of this effect with steric interaction of substituents leads to permanently nonplanar push-pull ethylenes in which the steric barrier is higher than the π-electron barrier[26-29].

Comparison of Solution and Solid State Conformations of Substituted Methylenemalonaldehydes

In spite of great endeavour and many monosusubstituted compounds tried, we did not succeed in preparation of monocrystals suitable for X-ray diffraction studies, probably due to the relatively low stability of these compounds. Thus, as the only

TABLE VI
Length of C=C bond and its torsion angle in some sterically crowded ethylenes

Compound	$l_{C=C}$, pm	Torsion angle, °
II	135·8	10·9
III	138·0	20·1
IV[a]	141·0	18·6
V[a]	141·2	31·2
VI[b]	136·5	36·2
VII[c]	139·0	43
VIII[d]	143·0	18·1
IX[e]	138·0	11
X[f]	140·5	47·2
XI[g]	135·3	19·7
XII[h]	135·7	28·6

[a] Ref.[32]; [b] ref.[33]; [c] ref.[34]; [d] ref.[35]; [e] ref.[36]; [f] ref.[37]; [g] ref.[38]; [h] ref.[39].

representative of the monosubstituted derivatives remained 2-thienylmethylene-malonaldehyde (*I*) whose spatial arrangement (particularly planarity) obviously differs from the conformation of benzylidenemalonaldehydes. According to the NMR measurements[30], the solution conformation of *I* resembles that in the solid state, not only in the arrangement of the formyl groups but also in the spatial relation of the thiophene ring to the Z-formyl oxygen. The conformational behaviour of monosubstituted methylenemalonaldehydes in solution was characterized on the basis of the solvent and temperature dependence of the $^1J(CHO)$, $^3J(CHO, CHO)$, $^3J(CHO, CH)$, $^4J(CHO, CHO)$ and $^4J(CHO, CH)$ spin–spin coupling constants[30].

The NMR spectral measurements on substituted benzylidenemalonaldehydes show that both the formyl group and the benzene ring are rotated out of the methylenemalonaldehyde plane. The conformation of both formyl groups is strongly correlated, the *trans–cis* arrangement being favoured, and conformation of the Z-formyl group is determined by its steric interaction with the aromatic nucleus.

In solution, monosubstituted methylenemalonaldehydes exist in the *s-cis*, *s-trans* conformation in which the steric interactions between the aryl (heteroaryl) and formyl, as well as the coulombic repulsion between the formyl oxygen atoms, are small.

Benzylidenemalonaldehydes represent a considerably flexible system in which the ratio of the most populated conformers *A* and *B* is influenced by substituents on the aromatic nucleus and the solvent[30] (Scheme 1).
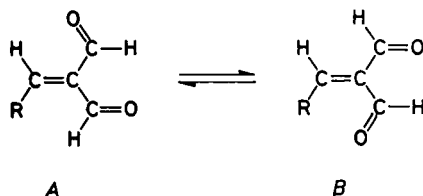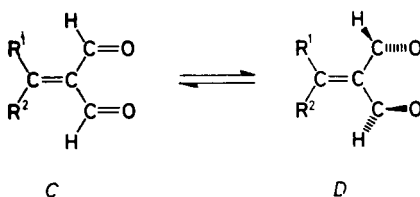

SCHEME 1

The rotation of the aryl (heteroaryl) groups from planarity was investigated using the long-range proton–proton spin–spin coupling constants. It is known[31] that the para-benzylic coupling ^6J between the α-proton of the side chain and the *para*-proton of the aromatic nucleus shows a simple conformational dependence (thanks to its insensitivity to substitution)[31]. The torsion angle of the phenyl group, as determined from the $^5J(CH, H_{arom})$ and $^6J(CH, H_{arom})$ values, depends on the position and steric demands of the substituent and ranges from 40° in benzylidenemalonaldehyde to 80° for the 2,6-dichloro derivative[19].

NMR studies[18,30] have shown an important difference in the steric situation in mono- and disubstituted methylenemalonaldehydes. Diarylmethylenemalonaldehydes exist as the *s-trans*, *s-trans* conformers (both planar and nonplanar). The conforma-

tional behaviour of these compounds has been determined by the solvent and temperature dependence of the ^4J(CHO, CHO) and ^3J(CHO, CHO) spin–spin couplings[18]. Disubstituted methylenemalonaldehydes exist in solution in two conformational types[18]: one with a nearly planar methylenemalonaldehyde moiety (C), favoured in polar and H-bonding solvents, and the other with strongly out-of-plane formyl groups (D), present in nonpolar solvents (Scheme 2).
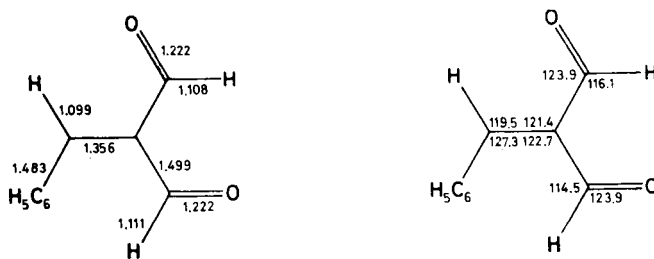

SCHEME 2

The nonplanar conformation, although energetically less stable, is strongly favoured entropically[17]. The planar form is stabilized by conjugation energy in the methylenemalonaldehyde moiety, on the other hand it is destabilized by electrostatic repulsion of the aldehyde oxygen atoms and by the aryl–formyl steric interaction.

The conformation of II and III found in crystal by X-ray diffraction, practically agrees with the solution conformation D. However, the NMR experiments give no information on the degree of nonplanarity of the formyl groups in solution and on the barrier between the planar and nonplanar conformers.

Quantum Chemical Calculations

The experimental data on spatial arrangement of the monosubstituted methylenemalonaldehydes were compared with the results of quantum chemical calculations. For benzylidenemalonaldehyde the possible conformers were optimized by several semiempirical (CNDO/2, INDO, MNDO) methods and by the ab initio method (in the STO-3G basis). All the methods led to the s-cis, s-trans conformation, in

SCHEME 3

accord with the ^{1}H and ^{13}C NMR spectroscopic results. The total optimization was performed by the MNDO method and the resulting parameters are given in Scheme 3. Like the experimental studies, quantum chemical methods indicate a considerable flexibility of this system: the calculated barriers to rotation of phenyl and formyl are low. In the optimum conformation the phenyl ring is rotated from the methylenemalonaldehyde plane by $65-85°$ and the torsion angle of the torsion angle of the carbonyl group amounts to $40-75°$. These results are in agreement with the conclusions made from the NMR spectral studies in solution.

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Translated by M. Tichý.