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AN NMR AND THEORETICAL STUDY ON THE CONFORMATIONAL BEHAVIOUR OF BENZYLIDENEMALONALDEHYDES. A CONFORMATIONALLY FLEXIBLE UNSATURATED SYSTEM

by

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Abstract - The conformational behaviour of the methylenemalonaldehyde fragment of the title compounds is characterized by solvent and temperature dependencies of $^1J(\underline{CHO})$, $^3J(\underline{CHO},\underline{CHO})$, $^3J(\underline{CHO},CH)$, $^4J(\underline{CHO},\underline{CHO})$ and $^4J(\underline{CHO},\underline{CH})$ spin-spin couplings as well some ab initio (STO-3G) and semi-empirical level molecular orbital calculations. The conformational behaviour of the couplings is also discussed on the basis of some INDO/FPT calculations. The conformations of the two formyls are strongly correlated, the trans-cis arrangements being favored. The conformation of the Z-formyl is determined by the steric interaction with the aromatic nucleus. The conformations of the formyls are sensitive to solvent and substitution on the aryl. Approximate populations and couplings of the sites are derived. There is some evidence about the non-planarity of the methylenmalonaldehyde fragment. Complex formation with $Mg(ClO_4)_2$ is reported.

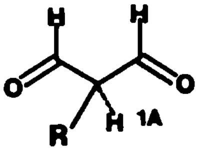
The structural and dynamical properties of malonaldehydes and related compounds are of considerable experimental and theoretical interest. In the case of malonaldehydes carrying at least one hydrogen atom on the carbon C(2) **1A**, most widely discussed problem is the formation and structure of the enolforms, stabilized by intra- (**1B**) or intermolecular hydrogen bonds (**1C**), typically dependent of not only substitution but also the medium.[1] By contrast, much less is known about the detailed arrangement of non-enolisable malonaldehydes. From these several disubstituted types have been described (dialkyl 2[2], arylalkyl 3[3], halogenmalonaldehydes 4[4]) but their conformational properties are not known. The exclusive existence of the dialdehyde form, stabilized by the intramolecular hydrogen bond, has been found with the compound **8**, which can be looked upon as phenylhydrazone of mesoxalic aldehyde.[5]

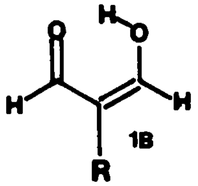
An interesting and essentially new group of non-enolizable α,β-dialdehydes are the substituted methylenemalonaldehydes (**6**,**7**). From these, only few have been mentioned earlier[6], but recently a general and simple approach has been developed both to benzylidenemalonaldehydes[7] 6 (R^1 = aryl) and diarylmethylenemalonaldehydes[8] 7 (R^1, R^2 = aryl). In this communication we describe some studies on the conformational behaviour of the methylenemalonaldehyde fragment in some aryl- and heteroarylmethylenemalonaldehydes and alkylidenemalonaldehydes (**6**).

To attack the problem the following strategy was applied: a) simple molecular mechanics and semiempirical and STO-3G MO calculations were used to characterize the principal components of the energetics of the system; b) by comparing the experimental and calculated dipole moments some constraints were derived for the possible conformations; c) the energetics were then characterized on the basis of the previous constraints and spin-spin couplings.

The simplest unsaturated aldehyde, acrolein **9**, has been shown experimentally to exist preferentially in the s-trans conformation, this being by 8 kJ/mol more stable than the s-cis-isomer.[9]

In accord with this finding are also the ^{1}H NMR[11] and proton coupled ^{13}C NMR spectra.[12] Molecular orbital calculations for the energy difference and the barrier have been also reported.[13] For cinnamaldehyde **10** it has been shown that both the E-isomer and the thermodynamically less favorable Z-isomer exist exclusively in the s-trans conformation.[14]


1A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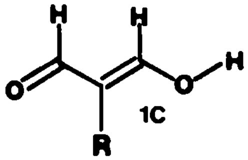
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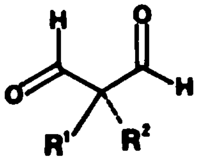
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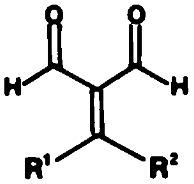
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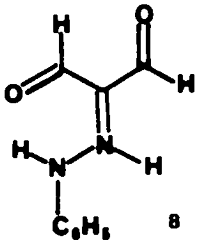
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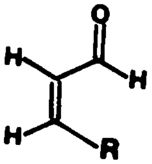

9-10

2; R^1, R^2 = alkyls
3; R^1 = alkyl, R^2 = aryl
4; R^1 = R^2 = halogen

5; R^1 = R^2 = H
6; R^1 = H, R^2 = aryl, heteroaryl, alkenyl
7; R^1, R^2 = aryls

9; R = H
10; R = Phenyl

The following compounds were prepared for this study:

6a; R^2 = phenyl
6b; R^2 = 4-methoxyphenyl
6c; R^2 = 4-nitrophenyl
6d; R^2 = 2,6-dichlorophenyl
6e; R^2 = 4-dimethylaminophenyl
6f; R^2 = 2-methylphenyl
6g; R^2 = 2-thienyl
6h; R^2 = 3-thienyl
6i; R^2 = $C_6H_5CH{=}CH$-
6j; R^2 = $EtOCO(CH{=}CH)_2$-

In our previous study on the conformational behaviour of diarylmethylenemalonaldehydes[15] we showed that the methylenemalonaldehyde fragment in those compounds is flexible and that the s-trans,s-trans (or briefly trans,trans) conformation is only slightly favored over the non-planar conformations. The trans,trans type conformation, with formyls about 20° out of the C=C plane for diphenylmethylenemalonaldehyde and the planar cis(E),trans(Z) arrangement for 2-thienylmethylenemalonaldehyde has been observed in solids.[16]

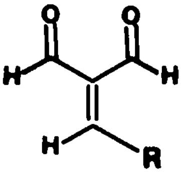
EXPERIMENTAL

Compounds **6a-6d**, **6f-6j** were synthetized as described in literature.[7,17] Compound **6e** was prepared as follows: 70% $HClO_4$ (0.5 ml) followed by 2-methylbenzaldehyde (1.20g, 10 mM) was added to an ice-cooled solution of 1,3-bis-dimethylaminotrimethinium perchlorate[18] (2.26g, 10 mM) in Ac_2O (15 ml). The reaction was stirred for 30 h at laboratory temperature, solid intermediate was precipiated and washed with dry ether, then stirred with dilute HCl (100 ml; 1:20) and benzene (50 ml) for several hours till dissolution. The product was isolated by extraction, drying the extracts over $MgSO_4$, evaporation of the solvent in vacuo and the product purified by chromatography on silica gel (dichloromethane). Crystallization from CCl_4 afforded 0.95 g (54.6%) of **6e**, m.p. 61-63°C. For $C_{11}H_{10}O_2$ calculated: 75.84 % C, 5.79% H; found: 75.69 C, 5.71% H. IR spectrum ($CHCl_3$, ν cm^{-1}): 2722 vw (C-H, CHO), 1742 w, sh, 1712 w, sh, 1695 s,sh, 1680 s (C=O), 1592 s (C=C), 1573 w, sh, 1480 w (ring), 1383 w (CH_3). ^{1}H NMR spectrum ($CDCl_3$), δ: 10.12 (CHO), 10.03 (CHO), 8.49 (CH), 7.2-7.5 (ring), 2.43 (CH_3).

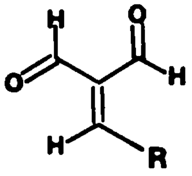
The ^{1}H and ^{13}C NMR spectra were taken on Jeol FX-60, Bruker AM-250 FT and Varian XL-200 spectrometers. Preparing the samples and running the spectra are described in our previous report.[15] A few coupled ^{13}C spectra were run by using the INEPT sequence.[19] The spectra were analysable by the first-order approximation. In some cases 2D NMR experiments were used to ensure the assignations. The dipole moments were determined as described in our previous work[15] and literature.[20]

MOLECULAR AND QUANTUM MECHANICS OF THE SYSTEM

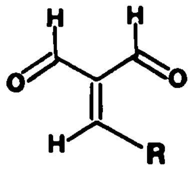
The energetics of the methylenemalonaldehyde fragment in **5** is controlled by several nearly equal energetical components. The conjugational energy difference between the cis and trans orientations of one formyl is expected to be ca. 8 kJ/mol[9,10] as in **9**. The trans,trans conformation is destabilized by an electrostatic repulsion between the oxygens. If the Scott-Scheraga molecular mechanics[21] and INDO level partial charges are applied, the oxygen-oxygen repulsion for the trans,trans conformer (5A) is 36, for *trans,cis* (5B) 26 and for *cis,cis* (5C) 23 kJ/mol. The formyl-aryl steric interactions are substantial for 6 and correlate with the aryl-ethylene torsion, the barrier of which may be expected to be rather close to that of styrene, about 16 kJ/mol[22]. This suggests that each of the four planar conformations **6A-6D** may be substantially populated in suitable conditions.



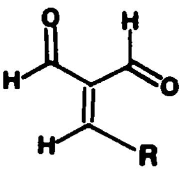
6A
trans(E),
trans(Z)



6B
cis(E),
trans(Z)



6C
cis(E),
cis(Z)



6D
trans(E),
cis(Z)

The oxygen-oxygen repulsion energy for the *up,up* arrangement (the formyls pointing to the same direction with torsion angles $\phi_E = \phi_Z = 90°$) is 31 and that for the *up,down* arrangement ($\phi_E = -\phi_Z = -90°$) 26 kJ/mol.

In order to estimate the total energetics of the system, the CNDO/2, INDO, MNDO and STO-3G energies of the basic substructure, methylenemalonaldehyde 5, were studied with complete geometry optimization. As to the planar conformations, the energy differences between the *trans,cis* and *cis,cis* forms were rather insignificant: 10.62, 1.35, -2.31 and 0.45 kJ/mol (by CNDO/2, INDO, MNDO and STO-3G). All the methods found the *trans,trans* conformation as the energetically least favourable with respect to the *trans,cis* arrangement: 7.01, 6.13, 6.86 and 9.50 kJ/mol. This can be understood as a manifestation of the Coulombic repulsion between the oxygens.

The rotation barrier of acrolein is 20.3 kJ/mol.[10] That of benzaldehyde[23] is 20.5 (by MW, 33.0 by DNMR[23]) and that of acetophenone[24] 22.4 kJ/mol (MW, 33.0 DNMR[24]). The STO-3G method overestimates all these MW barriers by about 25 %.[13,23-24] INDO gives nonplanar conformer of the minimum energy for both acrolein[13] and methylenemalonaldehyde[15] and the method cannot be considered as reliable in the present case. The STO-3G torsional barrier of one formyl in methylenemalonaldehyde is ca. 20 kJ/mol and the torsions are almost independent of each others.[25] The method predicts by 30% smaller dipole moments than INDO, the STO-3G Coulombic interactions being thus too small. This means that the real formyl torsion barriers in the benzylidenemalonaldehyde may be less than 15 kJ/mol, which allow significant non-planarity in presence of steric interactions with the side-chain.

In **6a** also the benzene nucleus is twisted out of the ethylene plane. The problem has been studied by measuring the long-range couplings between the vinyl and ring protons: the torsion angle or freedom appears to be clearly bigger than in styrene and according to the Scott-Scheraga molecular mechanics the angle is as large as 50°.[26] The twist in solid diphenylmethylenemalonaldehyde is 40-50° and also the formyls twisted 20° out of the C=C plane.[16]

Dipole Moments

The INDO method predicts the dipole moment of ethanal exactly (2.67 D). The calculated value of acrolein, 2.83 (or 2.47 for the s-*cis* conformer) is clearly smaller than the observed moment of 3.11 D.[9] The numbers in Table 1 are for 5. The calculations for **6a** gave 0.75 (INDO), 0.74 (MNDO) for *cis,cis*; 4.40 (CNDO/2), 4.13 (INDO), 3.98 (MNDO) for *cis*(E),*trans*(Z); 6.31 (CNDO/2), 6.01 (INDO) and 5.79 D (MNDO) for *trans,trans*. The INDO values for **6a** are significantly bigger than for 5. We assume that the INDO method for 5 gives the correct behaviour and ca. 10% too small estimates of the real moments of **6a**. The observed moment of **6a** is 4.12 D in CCl_4, suggesting that arrangements like *cis,cis*, *up,down* and *up,cis* are not favoured. Because also the *trans,trans* arrangement is almost absent in nonpolar medium the most probable arrangements are *trans,cis*, *up,trans* and *up,up*.

Table 1. The values of $^1J(\underline{CHO})$ and $^3J(\underline{CHO},\underline{CH})$'s of methylenemalonaldehyde and dipole moment (in D) as computed by the INDO/FPT and INDO/FPT-PRMO procedures.

ϕ_1	ϕ_2	(CHO)$_1$ ^1J	(CHO)$_1$ $^3J_{trans}$	(CHO)$_1$ $^3J_{cis}$	(CHO)$_2$ ^1J	(CHO)$_2$ $^3J_{trans}$	(CHO)$_2$ $^3J_{cis}$	dipole moment[a]
cis	cis	169.29	18.64	11.53	169.29	18.64	11.53	0.46
45	45	167.83	15.40	8.92	167.83	15.40	8.92	2.59
up	up	170.22	14.02	7.65	170.22	14.02	7.65	4.00
135	135	174.12	17.26	9.54	174.12	17.26	9.54	4.73
trans	trans	173.18	21.96	13.25	173.18	21.96	13.25	5.14
45	-45	170.09	15.22	8.79	170.09	15.22	8.79	0.05
up	down	172.15	13.96	7.61	172.15	13.96	7.61	1.66
135	-135	173.61	17.28	9.66	173.61	17.28	9.66	4.12
up	cis	167.45	14.79	7.75	173.09	17.61	11.24	2.11
trans	cis	172.40	21.85	12.96	173.54	17.99	11.33	2.91
up	trans	169.42	14.25	7.49	176.06	20.79	12.49	4.02
PRMO experiments: the π-core was kept restricted[b]								
cis	cis	165.30	14.05	5.52	165.30	14.05	5.52	0.46
cis	trans	166.23	10.97	4.50	164.92	14.54	5.81	2.91
trans	trans	162.16	11.69	4.80	162.16	11.69	4.80	5.14

[a] The observed dipole moment of benzylidinemalonaldehyde (**6a**) is 4.12 D.
[b] The p_z atomic orbitals were set restricted for the SCF calculations.

NMR SPECTROSCOPIC STUDIES

All the nine easily measurable $^nJ(\underline{HH})$ and $^nJ(\underline{CH})$ couplings of the methylenemalonaldehyde fragment are sensitive to the nature of the sidechain and to solvent. The couplings can be expected to be intrinsically independent of minor changes in the aryl and, excluding the $^1J(\underline{CHO})$'s, intrinsically solvent independent. Therefore the observed variations are mostly accounted for the conformational variations induced by solvent and the sidechain.

Analyses of Spectral Parameters

The assignments of the formyl signals were based on stereospecific couplings and were in some cases checked by decoupling experiments and for **6i** by using COSY, NOESY and CH-correlated 2D NMR experiments. One of the CHO protons is coupled to the ring ortho protons with up to 0.10 Hz couplings, which also disturb accurate determining of the other splittings of the proton. This kind of proximity coupling is possible for the Z-formyl. Similar up to (±)0.45 Hz coupling in ^{13}C signals were applied for assigning the ^{13}C signals. Because $^3J_{cis}$ is normally smaller than the corresponding $^3J_{trans}$, $^3J(\underline{CHO},\underline{CH})$'s were used in assigning the ^{13}C signals.

$^1J(\underline{CH})$'s and $^3J(\underline{CH})$'s are taken as positive. $^4J(\underline{HH})$'s can be either positive or negative[27,28]. In most cases one $^4J(\underline{HH})$ was very small and the $\underline{CH}$-signal unresolved due to many small long-range couplings with the ring protons, any simple spin-tickling experiments being impractical. We can, however, assume that $^4J(\underline{CHO},\underline{CHO})$ of the trans,trans form is ca. +3.7 Hz.[15] The trans,trans form complexes weakly with $Mg(ClO_4)_2$ and an addition of the reagent thus increases the coupling.[15] $^4J(\underline{HH})$'s were followed vs the reagent added and the experiment shows that $^4J(\underline{CHO},\underline{CHO})$ of **6a** in CD_3CN must be positive and, for example, that of **6h** negative.

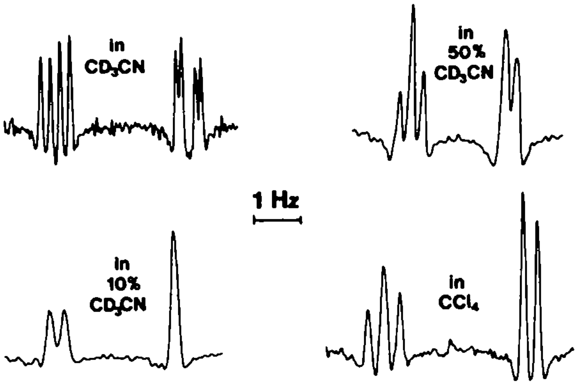


Figure 1. Solvent dependence of the formyl signals of **6e** when the CD_3CN/CCl_4 ratio is varied. The trapetzoidal window was used to resolve the splittings (no proper window in Jeol FX-60). The experiment shows that the interformyl coupling changes its sign when the CCl_4 concentration is increased.

Table 2. $^{4}J(\underline{HH})$'s (at 27 °C) of some substituted methylenemalonaldehydes $RCH{=}C(CHO)_2$.

Compound	R	Solvent	$^{4}J((C\underline{H}O)_Z,C\underline{H})$[a]	$^{4}J((C\underline{H}O)_E,C\underline{H})$[a]	$^{4}J(C\underline{H}O,C\underline{H}O)$[a]
6a	Ph-	CCl_4	+0.325	(-)0.315	-0.300
		C_6D_6	(+)0.391	(-)0.285	-0.109
		CD_2Cl_2	(+)0.285	(-)0.262	(-)0.070
		$CDCl_3$	(+)0.275	(-)0.214	$-^{c}$
		Ac-d_6	(+)0.439	(-)0.216	+0.102
		CD_3CN	+0.372	(-)0.206	+0.311
6b	4-H_3COPh-	CCl_4	(+)0.740	(-)0.215	-0.354
		$CDCl_3$	(+)0.573	(-)0.183	-0.072
		CD_3CN	(+)0.645	(-)0.135	+0.354
6c	4-O_2NPh-	$CDCl_3$	(+)0.525[b]	(-)0.305	-0.120
		CD_3CN	(+)0.554[b]	(-)0.234	-0.232
6d	4-$(H_3C)_2$NPh-	$CDCl_3$	(+)0.950	(-)0.090	-0.250
		Ac-d_6	(+)1.240	(-)0.095	(-)0.270
		CD_3CN	(+)1.100	(-)0.080	-0.165
6e	H_3CPh-	CCl_4	+0.391	$-^{c}$	-0.305
		$CDCl_3$	+0.303	$-^{c}$	$-^{c}$
		CD_3CN	+0.210	(-)0.134	+0.420
6f	2,6-diClPh-	CCl_4	(+)0.366	(-)0.242	(-)0.280
		C_6D_6	(+)0.390	(-)0.315	(-)0.159
		CD_2Cl_2	(+)0.280	(-)0.255	$-^{c}$
		$CDCl_3$	(+)0.305	(-)0.175	$-^{c}$
		Ac-d_6	(+)0.488	(-)0.260	$-^{c}$
6g	2-thienyl-	CCl_4	+1.724	$-^{c}$	-0.458
		C_6D_6	+1.739	$-^{c}$	(-)0.427
		$CDCl_3$	+1.630	$-^{c}$	(-)0.382
		CD_3CN	+1.723	$-^{c}$	(-)0.345
6h	3-thienyl-	CCl_4	+1.420	$-^{c}$	(-)0.402
		$CDCl_3$	+1.153	(-)0.121	(-)0.231
		CD_3CN	+1.111	(-)0.111	$-^{c}$
6i	PhCH=CH-	CCl_4	+2.508	$-^{c}$	(-)0.470
		$CDCl_3$	+2.301	$-^{c}$	(-)0.415
		CD_3CN	+1.910	$-^{c}$	(-)0.275
6j	EtOCO$(CH{=}CH)_2$-	$CDCl_3$	+2.169	$-^{c}$	(-)0.391

[a] The standard deviations as estimated directly from the spectra are about 0.010 Hz; [b] 0.020 Hz due to small couplings to ring protons.
[c] Not observable (usually smaller than 0.05 Hz).

Measuring the coupling in CCl_4, CD_3CN and various CCl_4/CD_3CN mixtures shows that the coupling of **6a** is negative in CCl_4 (see Fig. 1). The procedure was used to check the signs given in Table 1. Large $^{4}J((C\underline{H}O)_Z,C\underline{H})$'s are typical of the cis(Z) arrangement.[27] The $Mg(ClO_4)_2$ and solvent experiments indicate that $^{4}J((C\underline{H}O)_Z,C\underline{H})$ is positive for **6a**. $^{4}J((C\underline{H}O)_E,C\underline{H})$ did not change its sign in any experiment. Similarity of the pathway with ciscoid allylic[27], orthobenzylic[28] couplings and the corresponding coupling in acrolein[11] suggests that the coupling is negative.

The Cis(E),Trans(Z) = Trans(E),Cis(Z) Equilibrium; Behaviour of the $^{3}J(\underline{C}HO,\underline{C}HO)$'s

The $^{3}J(\underline{C}HO,\underline{C}HO)$'s can be used to probe the trans-cis isomerism of the individual formyls. The behaviour follows probably a Karplus relation with $^{3}J(\underline{C}HO,\underline{C}HO)_{trans}$ of ca. 4.5[15] and a minimum of ca. -0.5 Hz.[29] In **6e** $^{3}J(\underline{C}HO,\underline{C}HO)$ is close to the maximum. $^{3}J((\underline{C}HO)_E,(\underline{C}HO)_Z)$ and $^{3}J((\underline{C}HO)_Z,(\underline{C}HO)_E)$ and also the temperature and solvent induced changes in them are correlated: this is an evidence for the trans,cis = cis,trans type equilibrium and is a consequence and a manifestation of the Coulombic repulsion between the oxygens. For compounds with a bulky sidechain the cis(E),trans(Z) arrangement is predominant. For **6g**, **6i** and **6j** the trans(E),cis(Z) arrangement predominates.

Some values of $^{3}J(\underline{C}HO,\underline{C}HO)$ are very small, suggesting that the formyls may be clearly non-planar. This makes the discussion of the energetics difficult. Attempts to estimate the populations of the conformers and the off-planarity are discussed in their own sections.

Energetics of the Trans,Trans Form; Complex Formation with $Mg(ClO_4)_2$

An effective indicator of this conformer is a large $^{4}J(C\underline{H}O,C\underline{H}O)$. The coupling is assumed to be very sensitive to the simultanous planarity of the two formyls.[15] Our data show that the form is not

Table 3. $^{n}J(\underline{C}HO)$'s of some substituted methylenemalonaldehydes $RCH{=}C(CHO)_2$.

Compound R	Solvent	T °C	$^{1}J(\underline{C}HO)^{a}$		$^{3}J(\underline{C}HO,C\underline{H})^{b}$		$^{3}J(\underline{C}HO,C\underline{H}O)^{b}$	
			$(\underline{C}HO)_Z$	$(\underline{C}HO)_E$	$(\underline{C}HO)_Z$	$(\underline{C}HO)_E$	$(\underline{C}HO)_Z$	$(\underline{C}HO)_E$
6a Ph-	$CDCl_3$	27	181.11	183.46	10.48	7.15	0.86	3.34
	C_6D_6	27	180.79	182.82	10.48	7.27	0.80	3.10
		70	180.87	182.65	10.52	7.40	0.91	2.97
	Ac-d_6	27	181.68	182.96	10.46	7.59	1.21	2.98
6b 4-H_3COPh-	$CDCl_3$	27	179.62	180.92	10.29	7.60	1.22	2.83
		42	179.61	180.82	10.34	7.64	1.20	2.78
		61	179.72	180.78	10.42	7.75	1.34	2.66
6c 4-O_2NPh-	$CDCl_3$	27^{e}	182.89	185.87	10.43	7.31	0.77	2.87
	CD_3CN	27^{e}	184.17	185.28	10.43	7.74	1.46	2.78
6d 4-$(H_3C)_2$NPh-	$CDCl_3$	27	176.38	176.58	10.06	7.69	1.75	2.49
	CD_3CN	27^{e}	176.57	176.31	10.10	8.07	2.10	2.27
6e H_3CPh-^{c}	$CDCl_3$	27^{e}	181.42	184.25	10.33	6.53	0.45	3.83
	CD_3CN	27^{e}	182.12	183.44	10.29	7.15	1.15	3.62
6f 2,6-diClPh-	$CDCl_3$	27	183.44	185.61	10.82	6.75	0.67	3.22
	C_6D_6	27	183.05	184.96	10.72	6.87	0.80	2.81
		70	183.10	184.77	10.63	7.03	0.92	2.72
6g 2-thienyl-	$CDCl_3$	27	179.96	178.00	9.90	8.64	2.34	1.06
	Ac-d_6	27	179.68	178.26	9.88	8.93	2.70	0.65
		65	179.75	178.59	10.01	8.75	2.52	0.85
6h 3-thienyl-	$CDCl_3$	27	180.71	180.22	10.23	8.30	1.81	1.87
	CD_3CN	27^{e}	181.15	180.83	10.40	8.40	2.12	1.92
6i PhCH=CH-^{d}	$CDCl_3$	27^{e}	180.40	176.77	9.36	8.19	2.90	0.57
	Ac-d_6	27^{e}	180.18	178.27	9.56	7.79	2.64	0.97
	CD_3CN	27^{e}	180.43	178.73	9.61	7.78	2.65	1.27
6j EtOCO$(CH{=}CH)_2$-	$CDCl_3$	27	180.21	178.67	9.17	7.77	2.65	0.55^{a}

[a] The standard deviations of these couplings are about +0.10 (0.04 for those measured by using the INEPT sequence); [b] about 0.04 (0.02) Hz.

[c] $^{4}J((\underline{C}HO)_Z,\underline{H}_{ortho}) = \pm0.45(5)$ and $^{5}J((\underline{C}HO)_Z,C\underline{H}_3) = \pm0.10(2)$ Hz.

[d] $J((\underline{C}HO)_Z,C\underline{H}) = {}^{6}J(\underline{C}HO)_E,C\underline{H}) = \pm0.45(5)$ Hz, $^{4}J((\underline{C}HO)_E,C\underline{H}) = {}^{6}J((\underline{C}HO)_Z,C\underline{H}) = \pm0.48(5)$ Hz. The couplings are insensitive to solvent.

[e] Measured by the INEPT sequence.

predominant in any case. It is, however, the energetically most stable form of diarylmethylenemalonaldehydes[15], but for entropical reasons not the most populated. The positive $^{4}J(C\underline{H}O,C\underline{H}O)$'s in polar solvents suggest that the trans,trans form is present in some extent.

The complex formation free energies (at 300 K) with $Mg(ClO_4)$ were derived from seven $^{4}J(C\underline{H}O,C\underline{H}O)$ values by using the program EQUILA.[15] The complexes are weaker than those with diarylmethylenemalonaldehydes. Both 1:1 and 1:2 complexes may be formed[15]:

$$\mathbf{6a} + Mg(ClO_4)_2 \rightleftharpoons \mathbf{6a} * Mg(ClO_4)_2, \qquad \Delta G_1^\circ = -1.6(1) \qquad [i]$$

$$\mathbf{6a} + \mathbf{6a} * Mg(ClO_4)_2 \rightleftharpoons [\mathbf{6a}]_2 * Mg(ClO_4)_2, \qquad \Delta G_2^\circ = 4.5(20). \qquad [ii]$$

ΔG_2° is inaccurate (the concentration of **6a** cannot be accurately determined, due to instability of **6a**), but ΔG_1° is a good estimate. The bracketed numbers are the estimated standard deviations. Other model compounds and higher concentrations gave broadened lines. We had to assume ^{4}J of the complex to equal 3.7 Hz.[15] Without this assumption, poor estimates of the thermodynamic parameters are obtained, for the reasons discussed in ref. 15.

ΔG_1° of **7** is ca. -11 kJ/mol and ΔG_2° is -6 kJ/mol.[15] The difference of the free energies for **6a** is similar. The first step of the reaction [i] is

$$\text{"\underline{trans,cis}"} \rightarrow \underline{\text{trans,trans}}, \qquad \Delta G_3^\circ \qquad [iii],$$

("trans,cis" stands for the most stable form). If the free energy of the complexing step equals that of **7**, the trans,trans form is ca. 9 kJ/mol above "trans,cis". Because the trans,trans form is entropically less favorable, maybe by more than RT ln3 = 2.7 kJ/mol (at 300 K, if "cis,trans" is triple degenerate), the trans,trans form is energetically at most 6 kJ/mol above the other forms.

Assuming $^{4}J(\underline{HH})$'s intrinsically independent of the complexing we obtained estimates for the trans,trans conformation:

$$^{4}J((C\underline{H}O)_Z,C\underline{H})_{\underline{trans,trans}} = -0.250(25)\ \text{Hz}$$

$$^{4}J((C\underline{H}O)_E,C\underline{H})_{\underline{trans,trans}} = +0.110(40)\ \text{Hz}$$

About Energetics of the Cis,Cis Conformer; Four-Site Analysis

There is no coupling directly indicating the presence of the cis,cis form. Typical of this conformer is that both the $^3J(\underline{\mathrm{C}}\mathrm{HO,C}\underline{\mathrm{H}}\mathrm{O})$ couplings are simultanously small and that, the dipole moment of the form being relatively small, the population of the conformer is sensitive to polarity of solvent. Qualitatively, the conformer is quite possible for **6d**, and **6g**–**6j**.

If an equilibrium between four sites is assumed, the following relation is valid for any observed coupling:

$$ {}^nJ^i_{obs} = X_1\,{}^nJ^i_1 + X_2\,{}^nJ^i_2 + X_3\,{}^nJ^i_3 + X_4\,{}^nJ^i_4 \qquad [1] $$

where X_m is the molar fraction and ${}^nJ^i_m$ is the value of the coupling ${}^nJ^i$ for the site m. When the numbers of the observations and couplings are large enough, as in the present case, both the molar fractions and the unknown couplings are analysable from the data. The results of such an analysis is reported in Tables 4 and 5. The analysis was performed by the program MUSITE.[30] The rrms of 0.094 [= (sum of the residuals/the degrees of freedom)$^{\frac{1}{2}}$] is far worse than the estimated experimental values (from 0.01 to 0.04 Hz) and suggests that the model is not very good. Anyhow, Tables 4 and 5 show probably the best available estimates of ${}^nJ^i_m$'s and the molar fractions.

Without any constraints the analysis led to poorly defined sites. Therefore we did not used the $^1J(\mathrm{\underline{CH}O})$'s in the analysis of the molar fractions and for $^3J(\underline{\mathrm{C}}\mathrm{HO,C}\underline{\mathrm{H}})$'s a weight of 0.1 was applied. Otherwise the rrms would had been very bad due to the poor fit of ^1J's. We also kept some ${}^nJ^i_m$'s fixed, to avoid obtaining an unreasonably small $^4J(\mathrm{C\underline{H}O,C\underline{H}O})$ of the trans,trans form. In other words, the site is not statistically well defined. The constraints are descibed in details in Table 4. When the constraints were removed, the rrms was reduced only by a neglible amount.

Table 4 shows the values and "fits" (for definition see Table 4) obtained for ${}^nJ^i$'s. The fits are measures of how well obseved values are predicted by the model. They are different for each coupling and very poor for ^1J's. The fits for $^4J(\mathrm{C\underline{H}O,C\underline{H}O})$ and $^3J(\underline{\mathrm{C}}\mathrm{HO,C\underline{H}O})$'s are reasonable. Those for couplings involving $\mathrm{C\underline{H}}$'s are poor, implying that the couplings are effected by the nature and conformation of the aryl sidechain. As shown next, these couplings are sensitive to off-planarity of the formyls and this may explain a part of the poor fit. For these reasons the values for the couplings for the various sites should not be taken too seriously. The experiment shows that the system cannot be well described by the four-site model and the sites so obtained are not well-defined.

The molar fractions (Table 5) are more interesting. The data suggest that the cis,cis form is present in a substantial extent for the most compounds. The populations for the trans,trans form

Table 4. The values of couplings of the various sites as estimated by the four-site approach.

Parameter	Site				Fit[a] (Hz)
	s-trans(E), s-trans(Z)	s-cis(E), s-trans(Z)	s-cis(E), s-cis(Z)	s-trans(E), s-cis(Z)	
$^4J(\mathrm{CHO,CHO})$	3.70[b]	-0.35	-0.46	-0.58	0.02
$^4J((\overline{\mathrm{CHO}})_E,\mathrm{CH})$	0.11[b],[c]	-0.25	-0.25	0.11[b],[c]	0.13
$^4J((\mathrm{C\overline{H}O})_Z,\mathrm{C\underline{H}})$	-0.25[b],[c]	-0.25[b],[c]	2.59	2.58	0.17
[$^1J(\mathrm{CH\overline{O}})_E$	174.10	185.55	195.01	168.49	3.43][d]
[$^1J(\overline{\mathrm{CHO}})_Z$	180.21	181.12	192.59	174.41	3.33][d]
[$^3J((\overline{\mathrm{CHO}})_E,\mathrm{CH})$	8.38	7.01	4.90	9.98	0.60][e]
[$^3J((\overline{\mathrm{CHO}})_Z,\mathrm{C\overline{H}})$	9.89	11.00	8.97	9.34	0.39][e]
$^3J((\overline{\mathrm{CHO}})_E,(\overline{\mathrm{CHO}})_Z)$	4.50[b]	4.14	-0.10[c]	-0.10[c]	0.17
$^3J((\underline{\overline{\mathrm{C}}}\mathrm{HO})_Z,(\mathrm{C\underline{\overline{H}}O})_E)$	4.50[b]	0.00[c]	0.00[c]	4.48	0.05

[a] Fit = k * (sum of squares/number of the observed couplings)$^{\frac{1}{2}}$; k = (number of the equations/degrees of freedom)$^{\frac{1}{2}}$.

[b] These parameters were set to the values obtained by the $\mathrm{Mg(ClO_4)_2}$ experiment. Optimizing also them leads to a site not like trans,trans and does not improve the rrms substantially.

[c] These couplings were assumed to be independent of the conformation of the other formyl. Also this approximation has only a minor effect on the rrms.

[d] These parameters were calculated on the basis of molar fractions obtained by using the other couplings.

[e] These parameters were weighted by 0.1 in the calculations of the molar fractions, for similar reasons as given above. The couplings were not totally neglected in the fitting, because they are assumed to be different for each conformer and, thus, bring invaluable information about them.

Table 5. The populations of the various sites (at 27 °C) as estimated by the four-site approach.

Compound	R	Solvent	Populations (%) and relative energies (kJ/mol)[a]				Fit[b] (Hz)
			trans(E), trans(Z)	cis(E), trans(Z)	cis(E) cis(Z)	trans(E), cis(Z)	
6a	Ph-	$CDCl_3$	10(4.8)	70(0.0)	10(4.8)	9(5.2)	0.05
		Ac-d_6	12(4.0)	61(0.0)	12(4.2)	15(3.5)	0.17
6b	4-H_3COPh-	$CDCl_3$	8(5.0)	61(0.0)	11(4.2)	19(2.9)	0.12
6c	4-O_2NPh-	$CDCl_3$	7(5.6)	64(0.0)	19(3.1)	11(4.5)	0.20
		CD_3CN	5(6.7)	65(0.0)	2(8.3)	28(2.1)	0.12
6d	4-$(H_3C)_2NPh$-	$CDCl_3$	5(6.1)	55(0.0)	7(5.3)	34(1.2)	0.17
		CD_3CN	7(4.8)	47(0.0)	7(4.9)	39(0.4)	0.04
6e	H_3CPh-	$CDCl_3$	10(5.2)	77(0.0)	13(4.4)	0(-)	0.07
		CD_3CN	20(3.0)	65(0.0)	9(4.9)	6(6.0)	0.15
6f	2,6-diClPh-	$CDCl_3$	10(4.9)	69(0.0)	16(3.7)	6(6.3)	0.27
6g	2-thienyl-	$CDCl_3$	2(7.9)	27(1.6)	19(2.4)	51(0.0)	0.36
6h	3-thienyl-	$CDCl_3$	5(5.3)	43(0.0)	16(2.4)	36(0.4)	0.36
		CD_3CN	11(3.1)	38(0.0)	14(2.4)	37(0.0)	0.41
6i	PhCH=CH-	$CDCl_3$	3(7.6)	11(4.3)	25(2.2)	61(0.0)	0.14
		CD_3CN	6(5.5)	23(2.0)	19(2.5)	52(0.0)	0.32
6j	EtOCO$(CH=CH)_2$-	$CDCl_3$	3(7.2)	12(3.9)	29(1.7)	56(0.0)	0.29
		CD_3CN	5(6.7)	65(0.0)	2(8.3)	28(2.1)	0.12

[a] The bracketed numbers give the relative energies of the sites.

[b] The fits (see footnote a, Table 4) between the observed and calculated couplings for each case, excluding ^{1}J(CHO)'s. The fits include the ^{3}J(CHO,CH)'s without weighting (see footnote e, Table 4) and because the fits are rather poor for these couplings, the given total fits are overweighted by the these couplings.

are in accordance with previous discussions. The data also suggests that the fraction of the cis,cis form is decreased and that of the trans,trans form is increased in polar solvents. The molar fractions are not very sensitive to the approximations done for the coupling and, thus, can be assumed to be rather reliable. Anyway, the results suggest that the free energy differences between the four "principal" sites are not large and that each site is substantially occupied in some conditions or model compounds.

About Non-Planarity of Methylenemalonaldehyde Fragment; Behaviours of ^{1}J(CHO) and ^{3}J(CHO,CH)

The values ^{3}J(CHO,CHO)'s of (**6e**, **6i**, **6j**) are not typical of either trans- or cis-arrangements. The value of $^{3}J_{cis}$ in salicylaldehyde (that is chemically rather similar to the present system and with $^{3}J_{trans}$ like that of the present system) is as large as 1.53 Hz.[31] This suggests that the formyls are off-planar, which is supported also by the ^{1}J(CHO) and ^{3}J(CHO,CH) data, the previous theoretical considerations and the four-site analysis. For these reasons, we assume that the angles ϕ_E and, especially, ϕ_Z vary from compound to compound and from solvent to solvent.

$^{4}J((CHO)_E,CH)$ should be sensitive to the off-planarity of the E-formyl.[27] Because the observed couplings and the range are rather small and just for steric reasons, we suggest that the E-formyl is not strongly off-planar in any case.

An statistical average of the off-planarity for the present data can be roughly estimated from the fits (Table 4). The fit for $^{3}J((CHO)_E,(CHO)_Z)$ is not so good as for the other ^{3}J and suggest that the variation of ϕ_Z from the average value is bigger than that of ϕ_E. Assuming the coupling to vary as 4.5 * $\cos^2\phi$ and the average angles to equal 0° or 180°, the variation of ϕ_Z corresponding to the fit of 0.170 Hz is ca. 10°.

The ranges of ^{1}J(CHO) and ^{3}J(CHO,CH)'s are large and cannot be fully explained with solvent effects or electronic perturbations from the aryl periphery. In order to examine the effects of the conformational variations, some INDO/FPT level theoretical values (Table 1) were computed. The most remarkable trend is the sensitivity of the couplings to the planarity of the HC=C-CHO fragment. This is a consequence of the reduced conjugation of the double bonds: contribution of the π-system to the transmission of the spin-information is prevented in the non-planar arrangements. The mechanism can be probed by PRMO (Partially Restricted MO) calculations[32,33] by restricting the π-electron core before each SCF-cycle. As shown in Table 1, ^{3}J(CHO,CH)'s are greatly decreased by the restriction: the residuals represent the d-components of the couplings. The calculation implies that the $^{3}J(\underline{C}HO,C\underline{H})$'s measure the planarity of the formyls. Also the *trans-cis* isomerism of the formyl and that of the other formyl effect the couplings. The couplings have the maximum with the *trans,trans* arrangement. The four-site analysis supports the INDO/FPT model with a few execptions (which may be accounted for the incompleteness of the model): the ^{3}J's are bigger for the *trans*-arrangements and the *cis*-arragement of the other formyl decreases the coupling.

The experimental data support the non-planarity. For example, when $^{3}J((\underline{C}HO)_Z,(C\underline{H}O)_E)$ is small, indicating strong off-planarity of the E-formyl, also the corresponding $^{3}J((\underline{C}HO)_E,C\underline{H})$ is small. The trend is clear in Table 3. Unfortunately, this can be explained also by the *trans-cis* isomerism; also the off-planarity or the *cis*-arrangement (shown by $^{3}J((\underline{C}HO)_E,(C\underline{H}O)_Z)$) of the other formyl reduces the latter coupling.

The behaviour of $^{1}J(\underline{CH}O)$'s is more complex, although the conjugation of the π-system seems to be of importance. The effect can be interpreted as a spin-polarizability contribution of the π-system.[33] The most interesting values are those of **6c** and **6d**. On the grounds of the theoretical values, in the former both the formyls are simultanously planar and/or *trans*, and in the latter off-planar and/or *cis*. The other couplings and the four-site results being rather similar for **6c** and **6d**, a sound explanation with the nature of the *para*-substiteunts (see next) is that there is a clear difference in the planarities. The very large (and inaccurate) four-site values of $^{1}J(\underline{CH}O)$'s of the *cis,cis* site suggest that the conformation is more planar than the others.

The sidechain effect

The model compounds were chosen to represent several typical properties of the system. Some general trends can be derived: (*i*) the conformations of the formyls are correlated, most probably due to the Coulombic interactions; (*ii*) the conformation of the Z-formyl is determined by the sidechain and thus, determines the conformation of the E-formyl; (*iii*) the substitution on the sidechain effects the conformation of the malonaldehyde periphery.

The *para*-substituent effect is obviously a mixture of three contributions. First, the substituents effect the torsional freedom of the CH-ring bond; $N(CH_3)_2$ and OCH_3 increase and NO_2 lowers the barrier. The effects are as high as 50% for benzaldehydes[22] and acetophenones.[23] Because the higher barrier increases the planarity of the styrenoic system and thus the steric interaction with the formyls, $N(CH_3)_2$ should increase the proportion of the *trans*(Z) conformers or, when the forms predominating, off-planarity of the Z-formyl. The off-planarity is supported by the abnormally small $^{1}J(\underline{CH}O)$'s and the decreased $^{3}J((\underline{C}HO)_E,(C\underline{H}O)_Z)$ of **6d**. Second, $N(CH_3)_2$ is assumed to induce a substantial negative charge at the *ipso*-position (in respects of the vinyl), and thus, also favour *trans*(Z) over *cis*(Z). For NO_2 a reduced steric effect and positive charge are expected. These should favour *cis*(Z) over *trans*(Z), as supported for **6c** vs **6a**. Third, the electronic effect of $N(CH_3)_2$ strengthens the aryl-vinyl bond, weakening the C=C bond and thus maintaining the properties of whole the methylenemalonaldehyde fragment. This may explain a great deal of the poorness of the four-site fit.

CONCLUSION

The benzylidenemalonaldehydes form an interesting conformational problem. The s-*trans*,s-*cis* conformations of the methylenemalonaldehyde fragment are generally the most stable conformations due to the oxygen-oxygen Coulombic repulsion: the conformations of the formyls are correlated. *Cis*(E),*trans*(Z) is most stable for benzylidinemalonaldehydes and *trans*(E),*cis*(Z) for less bulky heteroarylmethylelenemalonaldehydes and alkylidinemalonaldehydes. The free energy of the planar *trans,trans* conformation is probably nearly 10 kJ/mol above the *trans,cis* conformers. There is no firm evidence for the existence of the *cis,cis* conformer. The present data also suggest that the system is rather flexible and that the non-planar conformations, especially for the Z-formyl, are probable. Another explanation of observed behaviour of $^{1}J(\underline{CH}O)$'s and $^{3}J(\underline{C}HO,C\underline{H})$'s is that substitution on the aryl has huge electronic effects through up to nine bonds.

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