A Nuclear Magnetic Resonance Study on Conformational Behaviour of Diarylmethylenemalonaldehydes and their Complex Formation with Magnesium and Lithium Perchlorates by using Four-bond Aldehyde Proton and Three-bond Aldehyde Carbon–Proton Spin–Spin Couplings; a Strategy for Studying Strongly Entropically Controlled Flexible Molecular Systems

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The conformational behaviour of the title compounds has been characterized by experiments based on the conformational dependence of spin–spin couplings. It is suggested that the compounds exist in two principal conformations: one with a nearly planar methylenemalonaldehyde fragment, favoured in the presence of polar, hydrogen-bonding, or complexing compounds like $CDCl_3$, $LiClO_3$, or $Mg(ClO_4)_2$ in CD_3CN; and the other with the formyl groups severely twisted out of the plane, favoured by non-polar or strongly protonating solvents. The non-planar conformation is energetically less stable but entropically strongly favoured. The conformational dependence of ^4J(C*H*O,C*H*O) and of ^3J(*C*HO,C*H*O) has been estimated on the basis of INDO/FPT level calculations and scaled by using the temperature- and solvent-dependence of the couplings. Complex formation with $Mg(ClO_4)_2$ and $LiClO_4$ and CD_3CN has been studied and the formation free energies are reported. The complexes are considered to be planar, with ^4J(C*H*O,C*H*O) 3.660(10) Hz and ^3J(*C*HO, C*H*O) 4.645(10) Hz. The value of ^4J(C*H*O,C*H*O) in cyclohexane can be as low as 0.440 Hz. The strategy and the use of the computer programs employed in data fitting are discussed.

Many conformational studies have been based on nuclear spin–spin couplings over three or four bonds. Although patterns of conformational behaviour of ^3J generally obey the Karplus relation,[1] the magnitudes of the components of the relation greatly depend on the chemistry of the fragment. Behaviour can be sometimes estimated from model compounds of rigid structure, and possibly refined by use of empirical substituent effects.[2] If no chemically similar, rigid compounds are available, temperature- or solvent-dependence of the spectral parameter can be utilized.[3,4] The same considerations are in principle valid for any molecular property. In many cases theoretical calculations of couplings at the INDO/FPT level[5] have provided reliable.

In the present report we describe some studies on a flexible novel chemical system, diarylmethylenemalonaldehyde.[6,7] The studies are based on the sensitivity of ^4J(C*H*O,C*H*O) and ^3J(*C*HO,C*H*O) (hereafter referred to as ^3J) to conformational changes in the methylenemalonaldehyde fragment. Because the system appeared to be flexible and similar, rigid model compounds were not available, the behaviour of the couplings was estimated by indirect methods. The value of ^4J in a possible class of model compounds, fuchsones,[8] appears to be about 2.5 Hz for the nearly planar conformer, whereas 3.660 Hz is suggested for our compounds. Approximate models of the couplings were obtained by using INDO/FPT calculations, complex formation with $Mg(ClO_4)_2$ or $LiClO_4$ in CD_3CN, and temperature dependence of the couplings. Temperature dependence of the couplings was used in the estimation of the conformational energetics, and indicates that the system behaves as if strongly entropically controlled. A strategy for the separation of the entropy and enthalpy contributions is described.

The observed couplings suggest that the methylenemalonaldehyde fragment may exist in two principal conformations: in a polar or complexing system the fragment is nearly planar, and in a non-polar system it is markedly non-planar. The coupling constants appear to be strongly solvent- and temperature-dependent. The temperature dependence can be explained either in terms of equilibrium between two or more sites, or of a strongly asymmetric and shallow potential minimum. It is also possible that the structure of the equilibrium conformation is solvent dependent, and that at least a part of the temperature dependence is due to the temperature dependence of the solvent dielectric constant. A description of the fragment by using molecular dynamics would demand averaging over the two torsion angles and would be rather difficult. In any case, the observed range of ^4J is so large in comparison with the theoretical range to be discussed later that one can speak without reservation about the planar and non-planar conformers. The ^4J coupling is sensitive to the planarity of the methylenemalonaldehyde fragment, which is also the most interesting conformational property of the system, and the main object of this study. The ^4J and ^3J data do not give a hint as to whether or not the oxygen atoms prefer the same side of the molecular plane. Therefore we define only two sites in which the system may exist. The various non-planar conformers and the notable temperature dependence of the couplings are accounted for by using an entropy-type free energy component between the two sites. In the following discussion we show that the temperature dependence of the spectral parameters can be satisfactorily interpreted within the two-site approximation. A simple dynamic model is also described.

Experimental

Materials and Methods.—The malonaldehydes (**1**) and (**3**)—(**5**) were synthesized as described in the literature.[6,7] Compound (**2**) was prepared as follows: silver perchlorate (0.91 g, 4.4 mmol) and calcium carbonate (500 mg) were added to a solution of 1,3-bis(dimethylamino)trimethinium perchlorate {[$(CH_3)_2$-

N–CH$\leq$CH–CH=N(CH$_3$)$_2$]$^+$ ClO$_4^-$}[9] (0.5 g, 2.2 mmol) in dry nitromethane (20 ml). The mixture was cooled to −35 °C and a solution of dichloro(4-fluorophenyl)phenylmethane (0.51 g, 2 mmol) in dry nitromethane was slowly added. The mixture was stirred with exclusion of air and light for 20 h, and the solid material was removed after addition of charcoal, by filtration through a layer of silica gel. Nitromethane was removed *in vacuo*. The solid intermediate was washed with dry ether (3 × 25 ml) and the residue stirred with a mixture of water (150 ml), perchloric acid (1 ml), and sodium chloride (5 g). The product was extracted with benzene–dichloromethane (5:1; 5 × 50 ml). The combined extracts were dried (MgSO$_4$) overnight, the solvents were removed *in vacuo*, and the product was purified by chromatography on silica gel (dichloromethane). Crystallization from cyclohexane–benzene afforded *4-fluoro-(α-phenyl)benzylidenemalonaldehyde* (**2**) (0.395 g, 77.7%), m.p. 129—130 °C (Found: C, 77.5; H, 4.3; F, 7.4. C$_{16}$H$_{11}$FO$_2$ requires C, 75.6; H, 4.4; F, 7.5%); $\nu_{max.}$ 2 768, 2 871 (CHO), 1 679, 1 719 (C=O), 1 420, and 1 602 cm^{-1} (rings); $\nu_{max.}$(CHCl$_3$) 2 743, 2 852 (CHO), 1 728, 1700, 1 667 (C=O), 1 601, 1 508, 1 445, 1 070, and 1 000 cm^{-1} (ring); δ(CDCl$_3$; Me$_4$Si) 7.10—7.63 (9 H, m, arom.) and 9.56 and 9.62 (1 H, d, CHO); *M*$^+$, 254.

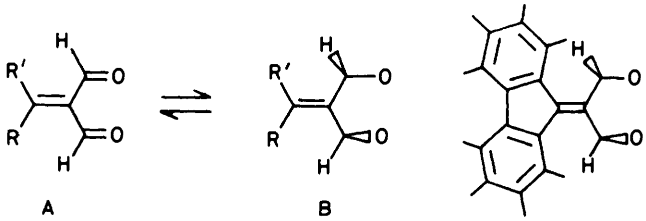
For ^{1}H n.m.r., solutions were 0.1—5% w/v; for ^{13}C n.m.r. 10—20% w/v solutions were used. The solutions were degassed with argon if removing a part of the solvent was not harmful. Dry LiClO$_4$ and Mg(ClO$_4$)$_2$ were prepared and dried as previously described.[10] The spectra were run on a JEOL FX-60 FT spectrometer by using a dual probe. ^{1}H N.m.r. spectra were measured for samples in 5 mm o.d. tubes, sometimes surrounded by an outer 10 mm o.d. tube containing the locking solvent or used to stabilize the sample temperature. The coupled ^{13}C n.m.r. spectra were measured for samples in 10 mm o.d. tubes, using the n.O.e. sensitivity enhancement. Temperatures were measured by the methanol method,[11] using a coaxial capillary tube. Data point resolution was maintained from 0.010 to 0.030 Hz. Spectral splittings are considered accurate within 0.010—0.050 Hz. In some cases [compounds (**2**) and (**3**)] very strongly second-order AB spectra or poor solubility in non-polar solvents resulted in relatively poor accuracies of spectral parameters. All the couplings are assumed to be positive.

Dipole moments of compounds (**1**) and (**6**) were determined for solutions in benzene and in CCl$_4$ at 25 °C by the method of Halverstadt and Kumler.[12] Usually, five solutions were prepared in the concentration range 2 × 10^{-3}—2 × 10^{-2} mol dm^{-3}. The permittivity was measured with a heterodyne instrument at 1.2 MHz, and the density was determined with an Oswald–Sprengel pycnometer. The molar refractivity was calculated using the Vogel increment.[13] The resulting error is insignificant in view of high dipole moment values, the accuracy of which can be considered to be 0.2 × 10^{-30} C m.

All the calculations were performed with a VAX 11/780 computer system. Standard geometry[14] and formyl geometry of ethanal[15] were used in INDO/FPT calculations by the program FINDO (Finn INDO).[16] Programs TWOSITE,[17] FUNNY,[18] and EQUILA[18] were used in iterative least-squares fittings of temperature and concentration dependence. The fitting programs are based on the Newton–Gauss iteration and are described briefly in the text.

Results and Discussion

Strategy.—The model compounds (**1**)—(**6**) were prepared. Experimental values of ^3J, ^1J, and ^4J are given in Tables 1 and 2 and they imply that the system is very sensitive to medium effects. Compounds (**2**)—(**5**) were used for studies on ^4J. Compound (**4**) was designed for the study of a marked non-planarity of the aryl system. Compound (**5**) was found useful because the chemical shift difference of the formyl protons is large enough to prevent tight AB systems, and it was more soluble than the other compounds in non-polar solvents. Compounds (**1**) and (**6**) were used only in ^3J experiments. Because the ^4J(C*H*O,C*H*O) values of compounds (**2**), (**3**), and (**5**) are very similar, the model compounds used were chosen on the basis of solubility, spectral properties, and availability.



(**6**)

Planar
s-*trans*.s-*trans*
$\varphi_1 = \varphi_2 = 180°$

Non-planar
$\varphi_1 = -\varphi_2$

(**1**) R = Ph, R′ = Ph
(**2**) R = Ph, R′ = 4-FC$_6$H$_4$
(**3**) R = Ph, R′ = 4-BrC$_6$H$_4$
(**4**) R = Ph, R′ = 2-naphthyl
(**5**) R = Ph, R′ = 2-thienyl

Scheme

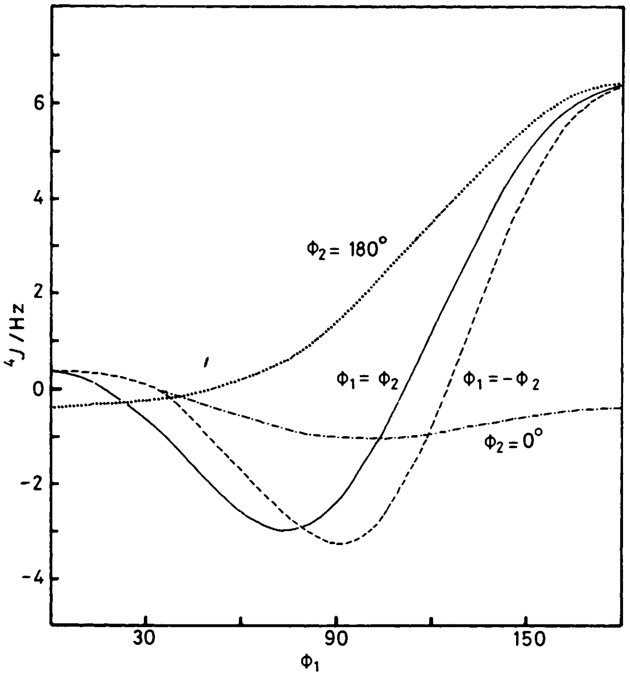


Figure 1. The conformational behaviour of ^4J(C*H*O,C*H*O) of methylenemalonaldehyde as computed by the INDO/FPT method. The torsion angle relationship $\varphi_1 = \varphi_2 = 180°$ corresponds to the W conformation

The following strategy was applied for the elucidication of the coupling behaviour and energetics of the system:

(i) The shapes of the coupling relations are assumed to be at least qualitatively predicted by the INDO/FPT model. This is supported by some calculations of ^4J couplings.[19,20] Computed couplings, INDO energetics, and dipole moments of methylenemalonaldehyde are shown in Figures 1—4.

(ii) Complexing with LiClO$_4$ or Mg(ClO$_4$)$_2$ in CD$_3$CN evidently favours a nearly planar W conformation. An analysis of the equilibria gives an estimate of ^4J in the complex and

Table 1. Values of $^1J(CHO)$ and $^3J(CHO,CHO)$ for some diarylmethylenemalonaldehydes in various solvents and at various temperatures

Compound	Solvent[a]	T/°C[b]	$^1J(CHO)$/Hz[c]	$^3J(CHO,CHO)$/ Hz[c]
(1)	[$^2H_6$]Benzene	75	181.823(50)	3.112(20)
		36	182.037(50)	2.869(20)
	[$^2H_6$]Acetone	65	182.165(50)	3.030(20)
		47	182.181(50)	3.103(20)
		29	182.099(50)	3.143(20)
	$CDCl_3$	60	182.719(50)	3.300(20)
		26	182.730(50)	3.565(20)
		−29	183.737(50)	3.976(20)
(4)	CD_3CN	27	182.615(50)	3.320(20)
	0.60M-$Mg(ClO_4)_2$[d]	27	195.880(50)	4.160(20)
	CD_3CN	27	183.130(70)[e]	3.390(50)[e]
			183.890(70)	3.070(50)
(6)	[$^2H_6$]Benzene[f]	27	183.600(100)	1.750(50)
	$CDCl_3$	60	183.575(50)	1.990(30)
		27	183.575(50)	2.060(30)

[a] Solute concentrations 10—20 w/v %. [b] ±1 °C. [c] The numbers in parentheses give the standard deviations in the last significant figure. They are estimated directly from spectra and vary owing to spectral properties. [d] 0.1M in 0.60M-$Mg(ClO_4)_2$–CD_3CN. [e] For the lower field formyl. [f] Broad lines: an unresolved *ca.* 0.3 Hz coupling possible to a ring proton.

Table 2. Values of $^4J(CHO,CHO)$ for some diarylmethylenemalonaldehydes in various solvents

Compound	Solvent	$^4J(CHO,CHO)$/ Hz[a–c]
(2)	[$^2H_{12}$]Cyclohexane	0.550(20)
	CCl_4	0.832(20)
	CS_2	0.930(20)
	[$^2H_6$]Benzene	1.365(30)
	Hexafluorobenzene	1.400(20)
	[$^2H_6$]Acetone	1.490(15)
	CD_3CN	1.737(10)
	3.35M-$LiClO_4$ in CD_3CN	3.033(15)
	1M-$Mg(ClO_4)_2$ in CD_3CN	3.650(20)
	$CDCl_3$	1.870(10)
(3)	CD_3CN	1.684(10)
(4)	$CDCl_3$	2.115(10)
(5)	[$^2H_{12}$]Cyclohexane	0.440(30)
	CCl_4	0.738(10)
	[$^2H_6$]Benzene	1.172(10)
	[$^2H_6$]Acetone	1.520(10)
	CH_2Cl_2	1.810(10)
	$CDCl_3$	1.810(10)
	[$^2H_4$]Methanol	2.000(10)
	10 v/v % HOAc in $CDCl_3$	1.965(10)

[a] At the ambient room temperature (28 ± 1 °C). [b] The numbers in parentheses give the standard deviations in the last significant figure. They are estimated directly from the spectra and vary from case to case owing to problems arising from solubility and/or a very tight AB system [compounds (2) and (3)]. [c] All couplings are assumed to be positive. The sign of the coupling in [$^2H_{12}$]cyclohexane, for example, must be the same as in $CDCl_3$, as shown in Figure 5.

thus in the nearly planar conformation. The lower extreme of the coupling in the non-planar conformation can be only roughly estimated by using temperature dependence and some constraints. The intrinsic effect of the complexing agent is considered to be small and negative, because it would be expected to follow the behaviour typical of the shape of the pathway.

(iii) The two-site approximation is used to describe the system quantitatively. Although the model cannot be very realistic in the present case, we consider that some essential properties of the system can be derived by inspecting the entropy difference between the sites. On the basis of solvent dependence we assume that the other conformer, favoured by polar and complexing

Table 3. Dipole moment measurements of some diarylmethylenemalonaldehydes

Compounds	Solvent	$10^{30}\mu_{exp}$/ C m	μ_{exp}/D
(1)	Benzene	19.28	5.78
	CCl_4	15.97	4.79
(6)	Benzene	14.41	4.32

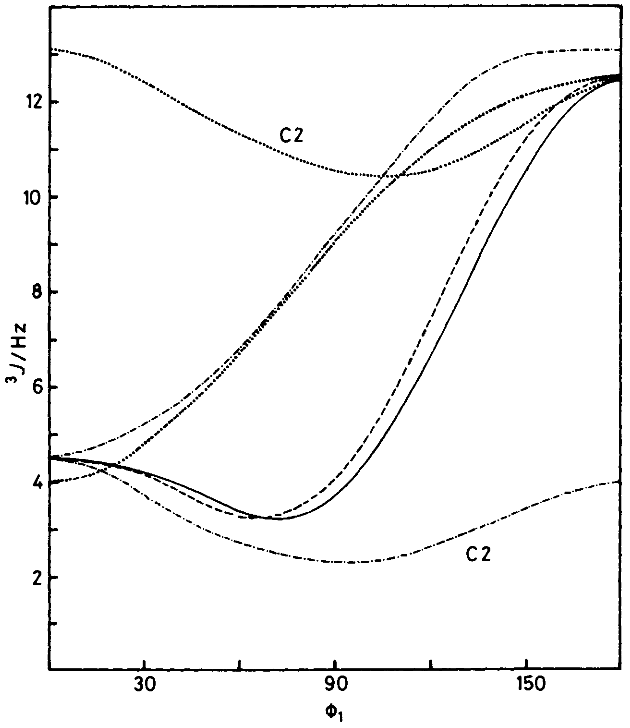


Figure 2. The conformational behaviour of $^3J(CHO,CHO)$ of methylenemalonaldehyde as computed by the INDO/FPT method. The symbols are defined in Figure 1; C2 refers to the coupling to the formyl proton that is not rotated

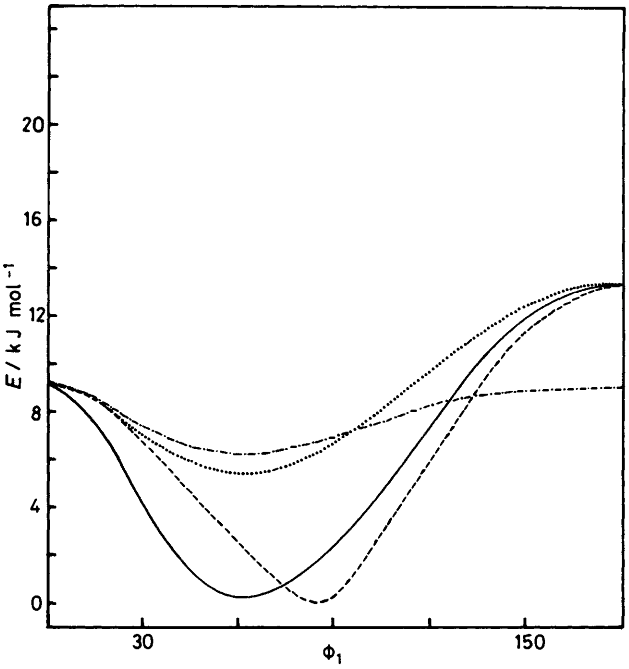


Figure 3. The conformational behaviour of the total energy of methylenemalonaldehyde as computed by the INDO approximation. The symbols are as in Figure 1

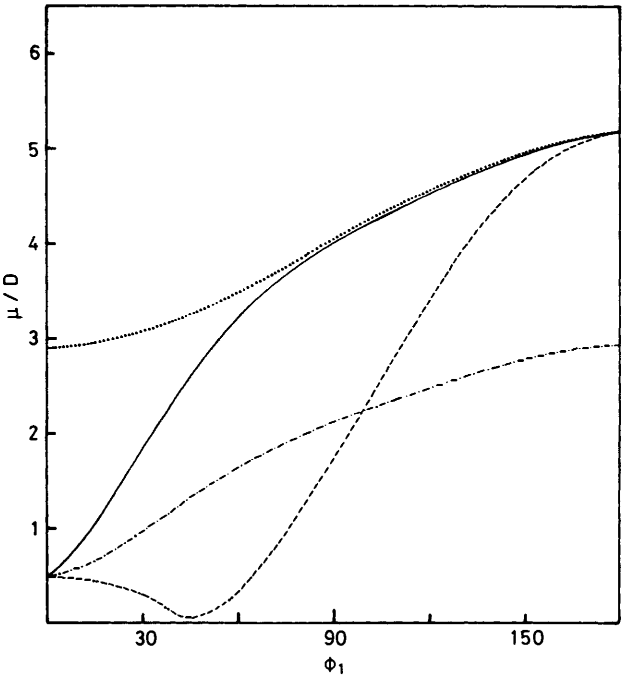


Figure 4. The conformation behaviour of the dipole moment of methylenemalonaldehyde as computed by the INDO approximation. The symbols are as in Figure 1

solvents, has a nearly planar W-type conformation, and the other a markedly non-planar conformation, favoured by non-polar solvents. For simplicity, only conformers with $\varphi_1 = \pm\varphi_2$ are considered. On the basis of INDO calculations (Figure 3), the non-planar systems $\varphi_1 = \varphi_2$ and $\varphi_1 = -\varphi_2$ are nearly equally stable for methylenemalonaldehyde. The smaller dipole moment of the latter conformation makes it favoured in non-polar media. On the other hand, the large dipole moments of (**1**) and (**6**), even in non-polar solvents (see Table 3), strongly indicate the coexistence of the $\varphi_1 = \varphi_2$ conformers. Details of the strategy are described in a later section.

Because the coupling constants of the $\varphi_1 = \varphi_2$ and $\varphi_1 = -\varphi_2$ conformations behave rather similarly, these two conformations are treated as one site, which is then entropically favoured if both conformations are substantially populated. The difference between the dipole moments in CCl_4 and in benzene is in agreement with the ^4J(C*H*O,C*H*O) information. By using temperature dependence of ^4J and ^3J of a few compounds in various solvents, expectation values of the couplings of the site conformations, as well as those of the enthalpy and entropy differences between the sites, are obtained.

The INDO/FPT *Model*.—On the basis of the INDO/FPT calculations, ^4J follows the patterns typical of propanoic and allylic systems.[19,20] For the present purpose only some characteristic correlated rotations of the formyl groups were computed; these are described in Figures 1—4. In practice many problems were met before appropriate conditions of convergence, especially for ^3J, were found: a perturbation parameter of 0.0001 (instead of default 0.001) and 75 FP cycles were to be used in the final computations. The absolute values of the couplings, especially those of ^3J, are increased by about 10% when the number of FP cycles is doubled. The behaviour appears to be typical of many formyl systems under study in this laboratory.[17] Although the INDO level energetics cannot be expected to be trustworthy, the dipole moments at the INDO level cannot be wrong in principle.

The formyl torsions can be described by angles φ_1 and φ_2; $\varphi_1 = \varphi_2 = 180°$ corresponding to the W conformer (in-plane conformer, s-*trans*,s-*trans* conformer). From Figure 1 it is clear that the dominating term of the coupling is proportional to $\sin^n(\varphi_1/2)\sin^n(\varphi_2/2)$. In fact, the 52 computed couplings in Figure 2 can be expressed by the analytical least-square formula (1) within r.r.m.s. = 0.129 Hz and r = 0.9991;

$$\begin{aligned}{}^4J(\varphi_1,\varphi_2) = {} & \mathrm{A}\sin^4(\varphi_1/2)\sin^4(\varphi_2/2) + \mathrm{B}\sin^2(\varphi_1/2)\sin^2(\varphi_2/2) \\ & + \mathrm{C}\sin^2\varphi_1\sin^2\varphi_2 + \mathrm{D}\sin\varphi_1\sin\varphi_2 + \mathrm{E}[\sin^2(\varphi_1/2) + \\ & \sin^2(\varphi_2/2)] \\ & + \mathrm{F}(\sin^2\varphi_1 + \sin^2\varphi_2) + \mathrm{G}\sin(3\varphi_1/2)\sin(3\varphi_2/2) \\ & + \mathrm{H}\,(\varphi_1\varphi_2/|\varphi_1\varphi_2|)\sin|2\varphi_1|\sin-|2\varphi_2| + \text{constant} \qquad (1)\end{aligned}$$

A = 3.687, B = 3.994, C = −1.657, D = 0.531, E = −0.752, F = −0.991, G = − 0.224, H = −0.621, and constant = 0.321. It is remarkable that the shapes of ^4J and ^3J resemble each other; using both of them does not essentially sharpen the picture obtainable from ^4J only. It is also clear that the couplings can be used to estimate only the importance of nearly W-type conformers, and that it cannot be decided whether φ_1 and φ_2 are of the same or of opposite sign.

The W coupling is clearly bigger than computed for propanoic or allylic systems[19,20] in accord with our experimental results. In order to compare the factors contributing to the maximum value, a number of INDO-FP-(D)NNBI,[16,20,21] INDO-FP-PRMO,[16,22] and INDO-FP-PRMO-NNBI[16] experiments were carried out (see Table 4). It has been previously shown by Barfield *et al.*[20] that the large W coupling is due to the vicinal *H**-*CO*-*CO*-*H* pathway (H* is the perturbed atom in FP calculations). If the Fock elements between the two carbons are set at zero, the present value is decreased by 3.569, in comparison with 2.690 Hz in the propanoic system.[20] Also another vicinal pathway *H**-(=*C*)-*CO*-*H*, with a contribution of 1.250 Hz can be shown. The trends can be explained by shortening of bond lengths by sp^2 hybridization. Because these properties are unique to the present chemical systems, it would

Table 4. INDO/FPT calculations on $^4J(CHO,CHO)$ of the methylenemalonaldehyde W conformation

NBIs[a]	RAOs[b]	^4J/Hz	Δ^4J/Hz[c]	Total energy/kJ mol^{-1} NBIs excluded	Total energy/kJ mol^{-1} NBIs included
		6.375	0.000	0.0	0.0
CH^*O/CH_2		6.188	0.187 (0.195)[d]	4.1 (1.0)[d]	−12.6 (−12.7)[d]
CH^*O/CH_2		6.143	0.232 (0.250)	5.2 (1.2)	−10.4 (−8.5)
$CH^*O,CHO/CH_2$		5.921	0.454 (0.435)	10.0 (2.3)	−20.4 (−16.8)
$CH^*O,CHO/CH_2$		8.918	−2.543 (−2.225)	130.2 (50.5)	−73.2 (30.9)
CH^*O/CHO		2.806	3.569 (4.125)	50.7 (11.9)	−32.2 (12.0)
CO/CO		5.853	0.522 (0.515)	0.3 (11.3)	−0.2 (−2.4)
CO/CO		3.395	2.980 (3.470)	41.0 (0.1)	−47.8 (0.1)
$CH^*O,CHO/{=}C$		5.384	0.991 (1.250)	32.3 (8.1)	−121.9 (−130.4)
	CH_2[e]	6.807	−0.432	0.0	0.0
	O,O	6.762	−0.387	0.0	0.0
	CH^*O[f]	5.392	0.984	0.0	0.0
	$=C$[g]	6.184	0.191	0.0	0.0
$CH^*O,CHO/CH_2$	CH_2	6.350	0.025	10.0	−20.4
$CH^*O,CHO/CH_2$	CH_2	9.207	−2.832	130.2	−73.2

[a] Non-bonded interactions set at zero. H* is the perturbed atom. [b] Restricted atomic orbitals. [c] Contribution of the interaction to the coupling. [d] DNNBI (Differential Neglect of NBI) calculation: the Fock elements are multiplied by 0.8 and the observed changes in the couplings and energies by 5.0. [e] $^3J(CHO,CH_2)$ was 1.812 (the standard calculation gives 6.929 Hz). This can be considered as a measure of the residual coupling.[16] [f] $^1J(CHO)$ was 89.318 (the standard calculation gives 173.180 Hz). [g] $^2J(CHO,C)$ was 7.208 (the standard calculation gives 8.177 Hz).

not be expected that any other chemical system could be used as a model for this case.

One interesting point is the contribution of the CH_2 group to the coupling. Our calculations show that its direct NBI contribution is small (only 0.454 Hz, as computed by the NNBI method). The CH_2 has, however, an indirect effect of −2.543 Hz through the interaction between CHO and CH_2 carbon atoms. Recent PRMO calculations imply that such calculations can be used to compute effects of spin-polarizabilities on couplings.[16] On trying to keep CH_2 restricted (this did not completely succeed; see Table 4) during the FP calculation (the PRMO method[16,22]) a contribution of only −0.432 Hz was observed. When both the Fock elements between H* and CH_2 are set at zero and CH_2 is kept restricted (the method can be called a PRMO-NNBI calculation), the direct NBI and CH_2 PRMO spin-polarizability contributions cancel and result in a change of 0.025 Hz in the coupling. It is interesting that the PRMO spin-polarizability effect of −0.289 Hz still appears when CH_2 is restricted after CHO/CH_2 NBIs are destroyed. These examples clearly show that the PRMO method, or any comparable procedure, cannot be used to replace the information obtainable by the NNBI procedure. Table 4 also contains some other pathside substituent PRMO spin-polarizability contributions. In order to discover the problem with the PRMO numbers, a case where *=C* or *C*HO was restricted was studied (Table 4): in both cases only surprisingly small changes in the couplings were observed, and the couplings to the restricted atom indicate that the atoms are substantially spin polarized during the last cycle, apparently by the help of spin-polarizations which have slipped through the restricted area during the previous cycles.[16]

Because the total energy of the present case (see Table 4) appeared to be sensitive to removing NBIs, and the total energy does not behave linearily as a Fock element is decreased, a modification of the NNBI procedure (DNNBI: Differential NNBI) was tested. In this method the whole of the off-diagonal Fock-element is not removed, in order to avoid large changes in the energetics of the system, but the elements are multiplied by a factor of, say, 0.8 and then an estimate of the total change in coupling is obtained by linear extrapolation to total removal of the element. The procedure gives a hint of what would happen if the overlaps were changed, for example chemically. In some case faster than linear decay of coupling was found.

The total energies as referenced to the standard calculation are also given: all the removed NBIs appear to be bonding (positive changes in the energy when the NBIs are excluded in the total energy calculation) but if they are included in the calculation (without SCF refinement) suprisingly large negative changes are induced. The latter property and the large differences between the NNBI and DNNBI energies can be explained by the flexibility of the electronic system: when a bonding interaction is removed it is compensated by some other interactions; the NBI energies are correlated. The NNBI and DNNBI coupling contributions are practically equal, suggesting, among other things,[16,20,21] that the NBI coupling contributions are not substantially correlated. This makes the meanings of the NBI coupling contributions very clear.

The computed ^3J follows a Karplus-type relation with a relatively large $^3J_{trans}/^3J_{cis}$ ratio and a relatively low minimum at about $\varphi_1 = \varphi_2 = 65°$, if both the formyl groups are out of plane. The relation with one of the formyl groups in-plane approaches the behaviour typical of some unsaturated systems.[23] The prominent $\sin^2\varphi$ contribution in these cases can be interpreted as a π-type component,[23,24] which operates when the other formyl is in-plane and thus forms a well defined π-electron system. The property makes the use of ^3J problematic, if it cannot be decided that both the formyl groups are simultaneously out-of-plane. This cannot be completely avoided even for the non-planar conformation, if it is defined as an average conformation with at least one formyl off-plane and with ^4J clearly smaller than that in the W conformation (as in the two-site approach). The average ^3J relation is probably a function with a very low or zero minimum. The value of the corresponding $^3J_{90°}$ in some aliphatic aldehydes is very near to zero, even negative.[17] A reasonable model system for the present case is salicylaldehyde,[25] with $^3J(CHO,C)_{trans}/^3J(CHO,C)_{cis} = 4.78/1.53$; these values are near to those suggested for the present system. In some monoarylmethylenemalonaldehydes,[26] ^3J can be as low as 0.45 Hz. To summarize, the average ^3J can hardly reach a value less than 0.0 Hz in the present system. One point typical of INDO/FPT results for formyl systems is that the method strongly

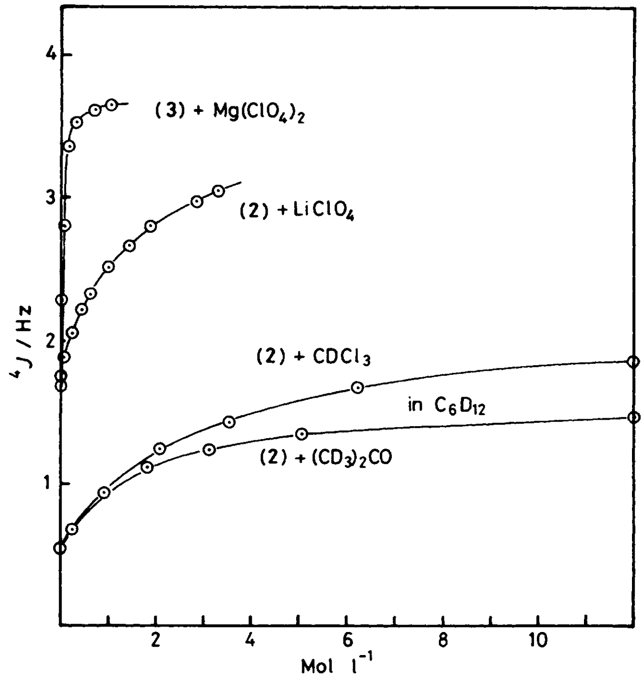


Figure 5. Concentrational dependence of ^4J of the compounds (**2**) and (**3**) at 300 K. The solubilities of the compounds were very low in cyclohexane and the concentrations were gradually increased (from 0.1 to 2 w/v %) at higher concentrations of the complexing agents to improve sensitivity. The $LiClO_4$ and $Mg(ClO_4)_2$ solutions in CD_3CN were *ca.* 0.2 and 0.1M and the concentrations were accurately determined for fitting with the program EQUILA

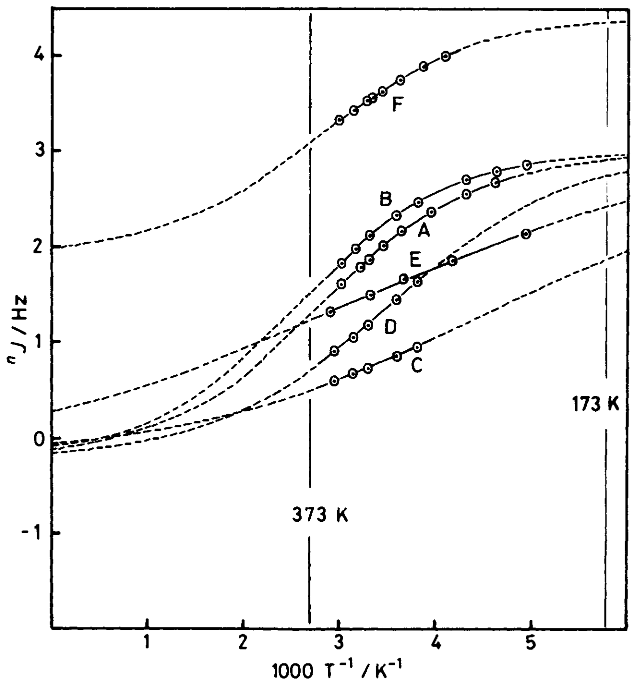


Figure 6. Temperature dependence of $^4J(CHO,CHO)$ and $^3J(CHO,CHO)$ of compounds (**1**), (**2**), (**4**), and (**5**) in various solvents as fitted by the two-site model (model *A*, Table 6): case A ^4J of (**2**) in $CDCl_3$; case B ^4J of (**4**) in $CDCl_3$; case C ^4J of (**5**) in CCl_4; case D ^4J of (**5**) in $CDCl_3$–CCl_4 (1:10); case E ^4J of (**5**) in $(CD_3)_2CO$; case F ^3J of (**1**) in $CDCl_3$. The spectra were run for *ca.* 5 w/v % solutions of the compounds

overestimates the range of ^3J; also the minimum value of the coupling is too large.[17]

The Maximum Value of ^4J *as Determined through Complex Formation with* $LiClO_4$ *or* $Mg(ClO_4)_2$.—Values of ^4J and ^3J in various solvents and at various temperatures are given in Tables 1 and 2 and Figures 5 and 6. The relatively large ^4J and ^3J in $CDCl_3$, the latter in comparison with salicylaldehyde,[24] are typical of the W conformation and suggest that the system is stabilized by a simultaneous hydrogen bonding of one $CDCl_3$ to two oxygens and by dipole interactions with $CDCl_3$. Several attempts were made to find a stronger complexing agent, and $LiClO_4$ and $Mg(ClO_4)_2$ dissolved in CD_3CN appeared to be able to control effectively the equilibrium between the planar and non-planar conformations. Both are strong complexing agents for diketones.[27] The strongly protonating solvents had not the same effect; each carbonyl may be hydrogen-bonded to one solvent molecule (methanol, acetic acid in $CDCl_3$) or even protonated (CF_3COOH, formyl signals strongly broadened).

The complexing reactions with M [= $LiClO_4$ or $Mg(ClO_4)_2$] can be approximately described by reactions (i)—(iv), with

$$A \rightleftharpoons B \qquad \text{(i)}$$

$$A + M \rightleftharpoons A{*}M \qquad \text{(ii)}$$

$$A + A{*}M \rightleftharpoons A_2{*}M \qquad \text{(iii)}$$

$$nM \rightleftharpoons M_n \qquad \text{(iv)}$$

corresponding free energy differences ΔG°_1, ΔG°_2, ΔG°_3, and ΔG°_4. The equilibrium (iii) was needed only for M = $Mg(ClO_4)_2$, and (iv) was used for M = $LiClO_4$ to describe the decay of the activity coefficient of M at higher concentrations. The expected value of the coupling, in the case of fast exchange between the sites, can be expressed in terms of the molar fractions X of the components as in equation (2), where A = planar and B = non-planar. If J were measured at various concentrations of the components, and also at a few temperatures, the thermodynamic parameters and spectral parameters, defined in equation (2), should be analysable from

$$J = X_AJ_A + X_BJ_B + X_{A*M}J_{A*M} \qquad (2)$$

the data. In this work we fitted the experimental concentration dependence of ^4J by use of the program EQUILA.[18]

The program EQUILA allows any ΔH°, ΔS°, or spectral parameter of a component, or a coefficient of a component in the reaction equations needed in the description of the equilibrium, to be refined to the least-squares criterion when parameters are given at various concentrations and temperatures. It is also possible to handle simultaneously several spectral parameters.[18] The solution is found iteratively, and the analysis, being fast, can be conveniently carried out under a time-sharing operation. The equilibrium equations can be defined in the input.

It was soon found that J_A and J_{A*M} cannot be simultaneously derived from our experimental data, and also that equilibria (iii) and (iv) are needed if almost complete fits are desired. Keeping J_A fixed during the calculation resulted in different thermodynamic parameters, but had no effect on J_{A*M} the main goal of the analysis. For these reasons we supposed that $J_A = J_{A*M}$. It also appeared that J_B cannot be fixed on the basis of the analysis, and that it has an effect only on the thermodynamic parameters. In fact, the A $\rightleftharpoons$ B system might be handled as one component: the question as to whether the free compound exists in one or in two conformations has no effect on ^4J_A. In the analysis shown in Table 5 we assigned to J_B values of 0, −1, and −2 Hz.

When the $LiClO_4$ data were fitted by using the equilibria (i)

Table 5. Complex formation parameters of $LiClO_4$, $Mg(ClO_4)_2$, $CDCl_3$, and [$^2H_6$]acetone with some diarylmethylenemalonaldehydes at 28 (± 1) °C as analysed by the program EQUILA

	$LiClO_4$, (2)			$Mg(ClO_4)_2$, (3) [or (1)][d]			$CDCl_3$, (2)	$(CD_3)_2CO$, (4)
	$^4J_B = 0$	$^4J_B = -1$	$^4J_B = -2$	$^4J_B = 0$	$^4J_B = -1$	$^4J_B = -2$	$^4J_B = -1$	$^4J_B = -1$
ΔG_1°	−0.45	0.69	1.46(11)[a]	−0.47	0.70	1.50(2)[a]	−1.75(2)[a]	−2.01(2)[a]
ΔG_2°	−2.70	−2.15	−1.84(84)	−12.36	−11.78	−11.47(22)	1.65(11)	1.20(30)
ΔG_3°	*b*			−7.05	−6.47	−6.16(29)		
ΔG_4°	0.16	0.00	−0.16(160)	*b*			9.05(89)	9.36(242)
n	1.40	1.40	1.40 (17)	*b*			3.13(14)	4.80(40)
^4J_A	3.813	3.813	3.814(93)	3.662	3.662	3.662(10)	3.660[c]	3.660[c]
r.r.m.s.	0.005	0.005	0.005	0.022	0.022	0.022	0.013	0.011
Points	10	10	10	8	8	8	7	6
^3J_A[d]				4.645	4.645	4.645(12)		
^3J_B[d]				2.225	1.564	0.903(45)		

[a] The numbers in parentheses give the standard deviation in the last significant figure as computed by the program EQUILA, the same for each ^4J_B. [b] No relevant value obtained for this case. [c] Kept constant. [d] $^3J(CHO,CHO)$ values were measured for (1) and ^3J values were estimated by using equilibrium constants of (3); the approximation may have a practical effect only on ^3J_B.

and (ii) only and keeping $J_B = -1$ Hz, then r.r.m.s. = 0.014 Hz and J_A = 3.459(13) Hz were found. Because the differences between observed and calculated values showed systematic variation, equation (iv) was tested (among other possibilities). By using $n = 2$, r.r.m.s. = 0.0054 Hz and J_A = 4.323(52) Hz were obtained. The refinement of n resulted in the values in Table 5. The equilibrium (iv) can be interpreted also as a model describing the decay of the activity coefficient of M at high concentrations of M (see Figure 5). The experiments with the various models suggest that the extrapolated value of J_A based on the $LiClO_4$ data is not accurate.

With $Mg(ClO_4)_2$ a much more complete complexation is obtained. If the secondary complex formation (iii), also found for $Mg(ClO_4)_2$ diketone complexes,[27] is not included, an unreasonable r.r.m.s. of 0.080 Hz is obtained. The final fit (0.022 Hz), much worse than in the $LiClO_4$ experiment, cannot be improved by including any simple equilibria; this can be explained by experimental problems arising from the small amounts of $Mg(ClO_4)_2$ used and the very tight AB spin system. An average chemical shift of 570.1 Hz (at 59.75 MHz) and a chemical shift difference of 3.484(10) Hz were obtained for (4) from 0.01M-solution in CD_3CN. The values for 0.01M-solution with 1M-$Mg(ClO_4)_2$ [with ^4J 3.650(30) Hz and thus almost completely complexed] are 540.9 and 1.976(50) Hz. The corresponding values for (2) in the $LiClO_4$ system are: 569.7 and 2.498(10) Hz for free (2), 546.0(5) and 1.75(10) Hz for the complex (as linear extrapolates of the chemical shifts *vs.* ^4J and assuming $^4J_{A\cdot LiClO_4}$ = 3.660 Hz). The effect of the nature of M on the chemical shifts is not large.

In order to show that the complexing is not necessarily the major reason for the conformational changes, excluding the cases of $LiClO_4$ and $Mg(ClO_4)_2$, the concentration dependences of ^4J in $CDCl_3$–[$^2H_{12}$]cyclohexane and [$^2H_6$]acetone–[$^2H_{12}$]cyclohexane are given in Figure 5. The experiments suggest that dipole–dipole interactions strongly control the system. Even a small amount of $CDCl_3$ or acetone greatly increases the solubilities of the compounds (which are very low and steeply decrease at lower temperatures) in cyclohexane. The concentration dependences was analysed by EQUILA; the results are reported in Table 5. If the change in the activity coefficient was not taken into account in the fitting, the following sets of r.r.m.s. and $J_{A\cdot M}$ were obtained: 0.017 and 2.154(16) Hz (for $CDCl_3$); and 0.019 and 1.604(15) Hz ([$^2H_6$]-acetone). When the decay of the activity coefficient [equation (iv)] was included in the model, r.r.m.s. was greatly improved, but very poor confidence limits were found. The phenomenon is the same as in the case of $LiClO_4$; $J_{A\cdot M}$ cannot be accurately extrapolated by the experiment. For these reasons $J_{A\cdot M}$ was fixed at 3.660 Hz, with the results given in Table 5. It is interesting that the decay in the activity coefficient of acetone follows a similar trend to that found in a study of conformational behaviour of 2-hydroxybenzylmethyl ether in acetone–CCl_4, with ΔG_4° = 23 kJ mol^{-1} and n = 5.1.[18] $^3J_{A\cdot M}$ and ^3J_B were estimated from values of ^3J of (1) in CD_3CN and in a concentrated $Mg(ClO_4)_2$ solution (Table 1) by using the complex formation parameters of (3). The results are given in Table 5.

On the basis of the present experiments we suppose that ^4J_A and ^3J_A are very near to 3.660 and 4.645 Hz, respectively, assuming that the complexing has no intrinsic effect on the values of the couplings. Furthermore the couplings do not have the same values in the planar conformation in $CDCl_3$ and in acetone solution, if the decay of the activity coefficient is taken into account. It cannot be proved that the complexes are strictly planar, but no substantial deviations from planarity are expected, because metal diketone complexes are planar, and a recent *X*-ray analysis of (1) shows that the oxygen atoms lie about 20° out of the methylene plane.[28]

Temperature Dependence of the Couplings: Two-site Approach.—In the two-site model, rigid conformers with a very high energy barrier between them and with a very fast exchange between the sites is assumed. In the present case the model is applied to a system of very flexible sites that are sensitive to medium interactions and separated by scarcely any barrier. When the sites are separated by a high barrier, each site is well defined. The extent of degeneracy and the widths of the potential minima contribute to the population of the site. The width of the minimum can be directly combined with the molecular entropy of the site and it can be shown also that the extent of degeneracy cannot be separated from the entropy contribution. When the sites are separated by no barrier at all, the conformation of the site becomes poorly defined. However, the following example and some comparisons (see later) with dynamic models imply that the two-site approach is sufficient to characterize some conformational properties. In the present case the planar site is defined as a group of nearly degenerate conformers with $\langle {}^4J \rangle$ (the expectation value of ^4J) *ca.* 3 and the non-planar site with $\langle {}^4J \rangle$ *ca.* −1 Hz. The main idea behind the following calculations is that the contributions of flexibility, low barrier, temperature-dependent solvent–solute interactions,[29,30] and ΔS are strongly correlated and can be combined in ΔS. If the formula given by Abraham *et al.*[30] is applied to solvent–solute dipole interactions in $CDCl_3$ or acetone, a contribution nearly

Table 6. The conformational energy components ΔH, ΔS, and ΔG at 25 °C (in kJ mol^{-1} or J K^{-1} mol^{-1}) and spectral parameters (in Hz) of some diarylmethylenemalonaldehydes as analysed by the two-site model

Parameter[a]	Case	Model						
		A[b]	*B*[c]	*C*[c]	*D*[c]	*E*[c]	*F*[d]	*G*[e]
$\langle ^4J_A \rangle$		3.00(6)	2.99(4)	3.03(5)	3.07(6)	3.11(7)	3.660	3.29(20)
$\langle ^4J_B \rangle$		−0.22(64)	0.000	−1.000	−2.000	−4.000	−1.000	−1.000
$\langle ^3J_A \rangle$		4.42(7)	4.41(6)	4.45(7)	4.47(7)	4.50(27)	5.03(15)	4.86(30)
$\langle ^3J_B \rangle$		1.92(5)	2.09(8)	1.32(12)	0.54(17)	−1.00(27)	1.15(26)	0.78(50)
ΔH	(1) or (2) and $CDCl_3$	10.1(13)	10.6(6)	9.1(7)	8.3(6)	7.5(6)	5.9(3)	6.19(87)
ΔS	(*A*,*F*[f])	28.5(65)	30.8(17)	22.6(16)	17.7(16)	11.8(16)	15.6(12)	
ΔG		1.64	1.40	2.34	3.01	3.95	1.22	
ΔH	(4) and $CDCl_3$ (*B*[f])	10.6(15)	11.0(8)	9.5(8)	8.6(9)	7.8(9)	5.0(3)	6.76(96)
ΔS		27.1(65)	29.3(25)	21.3(23)	16.5(23)	10.7(23)	11.0(11)	
ΔG		2.51	2.30	3.11	3.71	4.58	1.75	
ΔH	(5) and CCl_4 (*C*[f])	4.9(22)	5.9(5)	3.4(3)	2.7(3)	2.2(2)	3.1(6)	3.40(71)
ΔS		23.3(130)	28.8(19)	13.5(11)	7.5(9)	1.3(8)	14.5(20)	
ΔG		−2.04	−2.67	−0.63	0.45	1.76	−1.23	
ΔH	(5) and $CDCl_3$–CCl_4	8.9(23)	9.9(5)	7.18(4)	6.1(3)	5.2(3)	6.1(6)	4.52(75)
ΔS	(1:10) (*D*[f])	31.7(113)	36.1(16)	22.2(11)	15.7(10)	8.8(9)	21.2(20)	
ΔG		−0.48	−0.89	0.54	1.42	2.57	−0.21	
ΔH	(5) and $(CD_3)_2CO$	4.6(7)	4.9(s)	4.0(2)	3.6(2)	3.2(2)	3.1(3)	4.94(74)
ΔS	(*E*[f])	14.2(53)	16.2(8)	9.3(7)	5.3(6)	0.3(6)	9.1(10)	
ΔG		0.34	−0.39	1.21	1.99	3.05	0.36	
N_B	All	1.000	1.000	1.000	1.000	1.000	1.000	5.65(127)
r.r.m.s.		0.0162	0.0160[g]	0.0163	0.0171	0.0181	0.0334	0.0646

[a] The numbers in parentheses give the standard deviation in the last significant figure. When the standard deviation is not given, the parameter has been kept constant. [b] Model *A*: the fully optimized model. [c] Models *B*—*E*: $\langle ^4J_A \rangle$ kept constant. [d] Model *F*: $\langle ^4J_A \rangle$ and $\langle ^4J_B \rangle$ kept constant. [e] Model *G*: N_B set equal in every case and then optimized. ΔS set at zero. [f] The cases as in Figure 6. [g] The r.r.m.s. of model *B* is smaller than that of model *A* because the degrees of freedom of the simultaneous equations are less in model *B*.

linearly proportional to temperature is found. We assume that the sites are identical for all cases (solutions): in fact, we use the most representative, least-squares $\langle J_A \rangle$ and $\langle J_B \rangle$ values. This makes it relevant to compare the free energy difference components in the two cases.

The position and the temperature dependence of the $A \rightleftharpoons B$ type equilibrium is defined by ΔH, ΔS (enthalpy and entropy differences), N_A and N_B (degrees of degeneracy of the site). It must also be noted that ΔH is not necessarily constant.[29,30] Because ΔS and N_B (N_A can be set equal to 1) are fully correlated (the contribution of N_B to ΔS is equal to $R \ln N_B$, if $N_A = 1$) and if the temperature dependence of ΔH can be combined in ΔS, the total number of energy parameters needed to characterize the system is two. If $\langle J_A \rangle$ and $\langle J_B \rangle$ are known, it is easy to determine both ΔH and ΔS from the temperature dependence of J. It has also been shown[3,4] that up to three of ΔH, ΔS, $\langle J_A \rangle$, and $\langle J_B \rangle$ can be determined simultaneously if ΔH and ΔS are in certain ranges. The number of parameters to be determined from the temperature dependence of n.m.r. parameters can be reduced by assuming that $\Delta S = 0$, and fixing N_A and N_B on the basis of the structure, or by using $\langle J_A \rangle$ or $\langle J_B \rangle$ of a suitable model compound. In the present case we cannot even predict N_A and N_B, although it is probable that the number of planar conformers is smaller than that of the non-planar ones. This means that there are really four parameters (ΔH, ΔS, $\langle J_A \rangle$, $\langle J_B \rangle$) unknown for each temperature-dependent case.

Temperature dependences of ^4J and ^3J was measured in the cases given in Figure 6. The experimental results with theoretical fits are also shown in this Figure. If each of these six cases were separately fitted, the number of parameters to be refined would be 24; only 18 of these might be theoretically available in the situation where each case would produce three refined parameters. We can, however, assume that $\langle ^nJ_A \rangle$ and $\langle ^nJ_B \rangle$ are equal for all cases: in this way the definitions of the sites become the same for each case, as demanded by our strategy. When we also assume that ΔH and ΔS of (1) and (2) in $CDCl_3$ are equal, only 14 parameters are to be determined.

In practice the simultaneous optimization of the 14 parameters on the basis of 39 experimental couplings was carried out by the program TWOSITE.[17] By the program TWOSITE any thermodynamic and spectral parameters used in the model can be simultaneously optimized to the least-squares criterion. If some 'cases' are assumed to have a common property, ΔH, ΔS, or a spectral parameter, the cases can be handled simultaneously. Previously, a program for one case fitting has been discussed.[4] In the present case a three-parameter ($\langle ^3J_B \rangle$, $\langle ^3J_A \rangle$, and ΔH) fit, with $\Delta S = 0$ and $N_A = N_B$, results in very odd values, for example $\langle ^3J_B \rangle = -8.5$ Hz (for case F in Figure 6), proving that ΔS must be non-zero.

The optimization of the 14 parameters results in a minimum of r.r.m.s. of 0.016 Hz (see model *A*, Table 6), without substantial systematic deviations between computed and observed values. However, the value of $\langle ^4J_B \rangle$ is very weakly defined statistically by the experimental data used. This is shown by the statistics given by the program TWOSITE. For this reason we carried out some calculations keeping it at 0, −1, −2, and −4 Hz (see models *B*—*E*, Table 6). In model *F*, $\langle ^4J_A \rangle$ was kept at 3.660 Hz, the value obtained from the $Mg(ClO_4)_2$ experiment, and $\langle J_B \rangle$ was kept at −1 Hz because a convergence was not obtained for it. In model *G*, ΔS was set at zero and only N_B was optimized by setting $\langle ^4J_B \rangle = -1$ Hz. Although the r.r.m.s. values of cases *F* and *G* are not completely unreasonable, there are clear systematic deviations between observed and computed couplings.

The r.r.m.s. is only weakly dependent on $\langle ^4J_B \rangle$. This also means that the value of $\langle ^4J_B \rangle$ can be chosen rather freely to represent a typical non-planar conformation. There are reasons that make the best model, model *C* with $\langle ^4J_B \rangle = -1$, very reasonable. First, the minimum of the INDO/FPT ^4J value is *ca.* −3.5 Hz, and probably too low because the method seems to overestimate the extreme values of ^4J,[19,20] as it also does in the case of ^4J_A (assuming $^4J_A = 3.660$ Hz). Secondly, the non-planar site is an average conformation, and $\langle ^4J_B \rangle$ must be greater than the minimum ^4J value. The same considerations are valid for ^4J_A. Without any essential difficulties in the interpretation of the results we can assume that $\langle ^4J_B \rangle = -1 \pm 1$ Hz.

Another constraint is obtained from the behaviour of ^3J. The discussion on the INDO/FPT model for ^3J implies that it has no minimum or a very shallow one at φ = 60—70°. The ^3J value of (6) is practically temperature independent in $CDCl_3$ (see Table 1) and as small as 1.750 Hz in benzene. The compound is necessarily non-planar. Together with the value of $^3J_{cis}$ for salicylaldehyde (1.53 Hz) this suggests that $\langle ^3J_B \rangle$ can hardly be less than 0.5 Hz. According to Table 6, $\langle ^4J_B \rangle = -2$ Hz corresponds to $\langle ^3J_{off} \rangle = 0.54$ Hz if the energetics of (1) and (2) are assumed to be identical.

The bigger ΔS the more the non-planar conformation is entropy-favoured. Entropies of 10, 20, and 30 J K^{-1} mol^{-1} correspond to N_B values of 3.3, 11.1, and 36.9, respectively. The formal degrees of degeneracy of the non-planar conformers thus vary between 3 and 15, with fairly large confidence limits, if $\langle ^4J_B \rangle$ is assumed to be -1 Hz. The practically equal entropies of about 22 J K^{-1} mol^{-1} (model *C*) in $CDCl_3$ or in $CDCl_3$–CCl_4 suggest that the planar form in $CDCl_3$ is a 1:1 complex with a substantial negative entropy of formation. The entropy component also includes the temperature dependence of complex formation, which probably is responsible for a great deal of the temperature dependence of ΔG.

The hydrogen-bonding formation enthalpy of the planar $CDCl_3$ 1:1 association complex may hardly be bigger than the total hydrogen-bonding formation enthalpy of the possible non-planar $CDCl_3$ 1:2 complex if the hydrogen bonds are electrostatic in nature[31] and there is no borane-type stabilization in the planar $CDCl_3$ complex hydrogen bonding. However, ^4J and ^3J in $CDCl_3$ are substantially larger than in CCl_4 or in acetone. The explanation is that the 1:1 complex is entropically favoured. In CCl_4 there are no entropically unfavourable solvent–solute interactions, and the entropy difference is smaller (model *C*), corresponding to N_B about 3. The bigger values of ΔH and ΔG in acetone, in comparison with CCl_4, are explained by dipole interactions, which also operate through the formal ΔS because the interactions are proportional to the dielectric constant, which is increased at lower temperatures. The temperature dependence of the interaction should actually result in a bigger ΔS in acetone than in CCl_4. A smaller ΔS value is observed. Two contributions must be taken into account when an explanation is sought for the dilemma. First, the dipole moment of the $\varphi_1 = \varphi_2$ conformation is large over a wide range of φ and this conformation is not as sensitive as the $\varphi_1 = -\varphi_2$ conformation to solvent interaction or the temperature dependence of the interaction. On the other hand, the $\varphi_1 = -\varphi_2$ conformation is favoured in non-polar solvents and this increases the entropy of the non-planar site.

A Dynamic Approach.—If the potential over molecular co-ordinates is known, the corresponding population distribution over the co-ordinates can be estimated classically by using Maxwell–Boltzmann statistics. The expectation value of a spectral parameter can then be estimated if the corresponding spectral parameter function is known. Such a model, based on Maxwell–Boltzmann statistics, is called a dynamic model. A fairly complete description of the present system would demand integration over the four formyl and aryl torsion angles. In the following approach we describe a simple one-dimensional model and compare it with the two-site model. We assume $\varphi_1 = \varphi_2$ and equation (3), which follows the shape given by the INDO/FPT method and results in $^4J(180°) = 3.660$ and

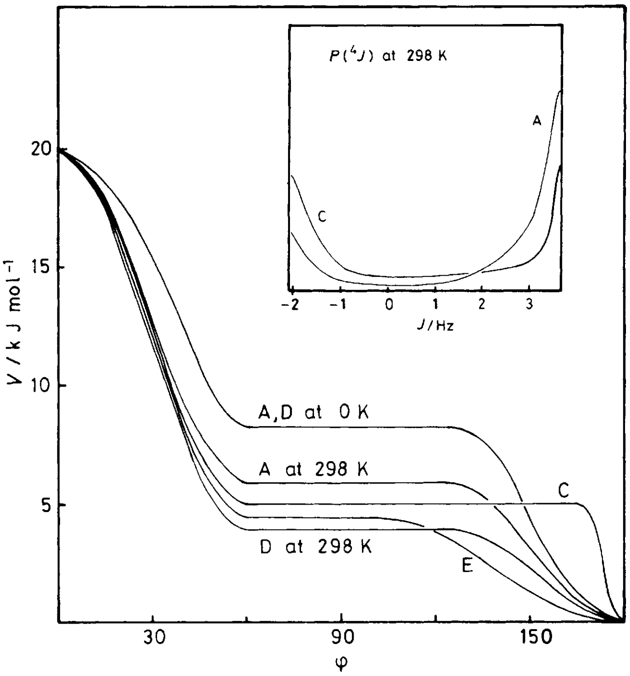


Figure 7. One-dimensional dynamic models of the cases A, C, D, and E, as defined in Figure 6 caption. The value of V (0°) is a rough one estimated by using simple molecular mechanics; $V(\varphi)$ decays to V(60°) as the $\cos^2$ function goes from 0 to 90° (the angle 60° is a rough estimate of the angle where the steric repulsions are nearly zero). From 60° to φ_x the value of $V(\varphi)$ is the potential parameter, which was optimized for each case by use of the program FUNNY. Also the angle φ_x was optimized. The potential decays to 0 as $\cos^2$. The cases A and D were assumed to have the same φ_x and the same potential parameter: only the temperature-dependent components of the potentials were independently adjusted. The insert shows the populations of conformers corresponding to the different values of ^4J as computed for cases A and C using the optimized potentials

$$^4J(\varphi) = 1.830\sin^8(\varphi/2) + 1.830\sin^4(\varphi/2) - 2.572\sin^2\varphi \quad (3)$$

$^4J(90°) = -2.000$ Hz. Potentials $V(\varphi)$ were adjusted to the program FUNNY[18] to give the least-squares fit between the observed and calculated ^4J values. The program and a detailed example are described elsewhere.[18]

The principal difficulty of this approach is that very many types of potential may give a good fit. Sometimes the potential can be composed of components derived from the structure or roughly estimated by molecular orbital theory or molecular mechanics.[18] The coefficients of the components can then be optimized. In the present case we can only assume that V(0°) is about 20 kJ mol^{-1} higher than V(180°), as suggested by simple molecular mechanics based on the Scott–Scheraga parametrization[32] for steric interactions and styrene torsion potential[33] for the aryl torsions. In order to examine a system in which there is no barrier between the non-planar and planar sites we used the potential defined in Figure 7.

The correspondence between the two-site and dynamic models is not straightforward in the present case. For the $CDCl_3$ case we did not find a good fit by using one simple function. Using more complicated expansions always led to a clear barrier between the sites. This was accounted for the temperature dependence of $V(\varphi)$; the temperature dependence was therefore set linearly proportional to temperature and the corresponding parameter optimized. The potential given for $CDCl_3$–CCl_4 was not well defined (the confidence limits of the two optimized parameters were large) and it was assumed that $V(\varphi)$ of the case of 0 K is the same as that of the $CDCl_3$ case.

Both the cases were then simultaneously fitted with two common potential parameters. The large entropy component of the two-site model then appeared as the temperature dependence of the potential. In the case of CCl_4 the potential can be assumed to be temperature independent: the entropy term appears as the wide flat potential section and the very steep potential minimum. When the same approach is used for the acetone case, the potential shown in Figure 7 is obtained. The differences between the CCl_4 and acetone potentials nicely reflect the differences in the two-site energy components (Table 6). The dynamic presentations may be more easy to understand than the two-site numbers, but one must remember that many other potentials give a good fit: only qualitative decisions can be made on the basis of the present model.

When the population distribution functions $P(^4J)$ (the populations of the conformers *vs.* the values of ^4J) are computed from $P(\varphi)$, the angular population distribution function, [corresponding to the optimized $V(\varphi)$], the presentation given in the Figure 7 insert is obtained. The insert suggests that, even if the barrier is low or does not exist, there may be two well defined '^4J states.' In the present case the ^4J states are also conformationally well characterized: the state with ^4J of -1 to -2 Hz represents the non-planar and other than the W-type planar conformers, and the other state represents the nearly planar W conformers. The two-site free energy components can then be related to the expectation values of the energy components between the two ^4J states. Without further experiments, more or more precise information can scarcely be derived from the present data.

Conclusions

All the n.m.r. experiments described in this work imply that the conformational energetics of the methylenemalonaldehyde fragment behave as if strongly entropically controlled. Clearly there exists a nearly planar *s-trans*, *s-trans* (W-type) conformation which is stabilized in polar or complexing media. It is likely that the planar conformation is more rigid than the non-planar representation, owing to repulsions between the formyl and aryl groups: the strong entropy control is maintained by the aryl periphery. The planar conformation is stabilized by the conjugational energy in the methylenemalonaldehyde fragment, which is, however, balanced by a strong electrostatic repulsion between the oxygen atoms and by the aryl–formyl repulsion, resulting in a decreased aryl–ethylene conjugation energy which is, however, disturbed also by aryl–aryl steric interactions. Thus, the molecular rotations are strongly correlated (co-operative). The electrostatic repulsion between the oxygen atoms, as calculated by the Scott–Scheraga molecular mechanics[32] by using INDO partial charges and the geometry previously described, is as large as 32 kJ mol^{-1}. On the basis of the present experiments it remains open how strongly the formyl groups are twisted out of the plane in liquid medium, and how high is the barrier, if any, between the planar and non-planar conformers.

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