Conformational Studies by Dynamic Nuclear Magnetic Resonance. Part III.[1] Rotamers arising from Restricted Motion in Substituted Benzaldehydes

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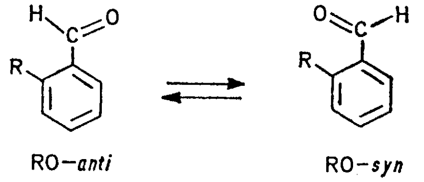
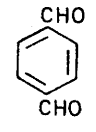
Rotational isomers due to the restricted motion of the formyl group have been unambiguously detected in *ortho*-substituted benzaldehydes. The conformers with the *ortho*-group and formyl oxygen *anti* have been shown. through ^{1}H and ^{13}C n.m.r. spectroscopy. to be the more stable species. the relative abundance depending on the bulkiness of the substituents. Thermodynamic activation parameters have been also obtained by computer simulation of the spectral lines. and a rotational model is proposed to rationalize the dependence of $\Delta G^{\ddagger}$ on the steric hindrance of *o*-alkyl groups. Proof of the existence of *cis*- and *trans*-isomers in terephthalaldehyde has been provided by means of liquid crystal n.m.r. spectra as well as by low temperatures n.m.r. measurements. Comparison has been made between this result and that of an e.s.r. conformational investigation on the corresponding radical anion obtained by photolytic as well as by chemical reduction.

RESTRICTED rotation of the formyl group in benzaldehyde has been unambiguously detected[2] by ^{1}H and subsequently by ^{13}C n.m.r.[3,4] spectroscopy. The free energy of activation ($\Delta G^{\ddagger}_{c}$) for the rotational process as estimated at the coalescence point,[2,3] agrees with the results of a total line shape analysis carried out[4] on ^{13}C n.m.r. spectra, despite the fact that in the three experiments reported different solvents were used. This independence of the medium suggests that the process is almost entirely intramolecular; as further support for this hypothesis the activation entropy was found to be negligible.[3,4]

The existence of relatively high activation energy for internal rotation in benzaldehyde should make possible the detection of rotational isomers in asymmetrically substituted derivatives, as discovered for other aromatic aldehydes.[5] This paper reports the detection of such conformers, the assignment of their structure, and the determination of their interconversion barriers. We found that *o*-alkyl substituted benzaldehydes (I)—(IV) represented the most suitable series for this study.



(I) R = Me
(II) R = Et
(III) R = Pr^i
(IV) R = Bu^t



(V)

Furthermore, attempts have been made to identify the two isomers of terephthalaldehyde (V) which, according to the arguments above, is expected to exist in *cis*- and *trans*-conformations. The two rotamers had been identified[6] by means of e.s.r. spectroscopy in the radical anion, but not yet detected in the neutral molecule.

RESULTS AND DISCUSSION

Whereas ^{13}C n.m.r. spectroscopy was very convenient for studying the rotational barrier in unsubstituted, or symmetrically substituted benzaldehydes,[3,4] ^{1}H n.m.r. spectroscopy (at 100 MHz) was found more suited for investigations of the alkyl-substituted derivatives (1)—(IV). At low temperatures, the chemical shifts of the formyl proton are sufficiently different to the *anti*- and *syn*-rotamers to be resolved at 100 MHz.

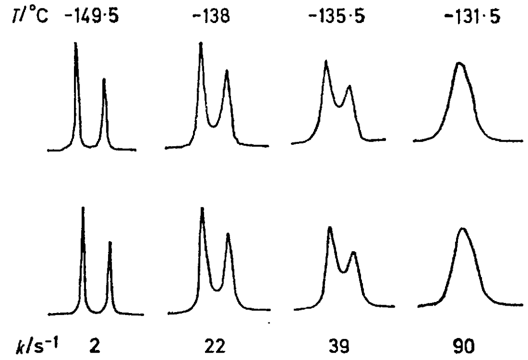


FIGURE 1 Experimental (top) and simulated (bottom) 100 MHz n.m.r. spectra of the formyl region of *o*-methylbenzaldehyde (I) taken at various temperatures in CHF_2Cl as solvent

As an example we discuss in some detail the case of compound (I) whose spectrum can be analysed accurately. In CHF_2Cl solution at -150 °C two signals separated by 40.0 Hz can be observed for the formyl proton, the downfield being more intense (60%) than the upfield peak.

At higher temperatures (Figure 1) the signals broaden

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[1] Part I *Tetrahedron Letters*, 1975, 1205; Part II, *J. Org. Chem.*, 1975, **40**, 2979.

[2] F. A. L. Anet and M. Ahmad, *J. Amer. Chem. Soc.*, 1964, **86**, 119.

[3] T. Drakenberg, R. Jost, and J. Sommer, *J.C.S. Chem. Comm.*, 1974, 1011.

[4] L. Lunazzi, D. Macciantelli, and A. C. Boicelli, *Tetrahedron Letters*, 1975, 1205.

[5] K. I. Dahlqvist and S. Forsén, *J. Phys. Chem.*, 1965, **69**, 4062; 1969, **73**, 4124; L. Arlinger, K. I. Dahlqvist, and S. Forsén, *Acta Chem. Scand.*, 1970, **24**, 662, 672; D. J. Chadwick, G. Meakins, and E. E. Richards, *Tetrahedron Letters*, 1974, **36**, 3183; D. J. Chadwick, *Tetrahedron Letters*, 1975, 679.

[6] E. W. Stone and A. H. Maki, *J. Chem. Phys.*, 1963, **38**, 1999.

and eventually coalesce into a single line at *ca.* −133 °C. In the slow exchange region, where both peaks are sufficiently separated, the relative intensities could be measured as function of temperature, the $\Delta G°$ values were therefore obtained and $\Delta H°$ as well as $\Delta S°$ determined (Table 1). The ratios were then extrapolated into the fast exchange region and in this way the kinetic constants over the whole interval where the exchange phenomenon is measurable were extracted. The total line shape method proposed by Binsch was employed and the computer simulations (some samples are given in Figure 1) are the output of the DNMR II program.[7] Measurements were carried out at nine temperatures in the interval −150 to −130 °C. The thermodynamic parameters of activation are also reported in Table 1. As observed for a number of molecules with internal motion the activation entropy ($\Delta S^{\ddagger}$) is negligible within experimental error, so that the more accurately determinable $\Delta G^{\ddagger}$ is used in the following discussion instead of $\Delta H^{\ddagger}$.

TABLE 1

Thermodynamic parameters for the forward equilibrium RO-*anti* $\rightleftharpoons$ RO-*syn* in *o*-methylbenzaldehyde (I)

$\Delta H°$/kcal mol^{-1}	$\Delta S°$/cal mol^{-1} K^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}
+0.55 ± 0.05	+3.7 ± 0.4	7.06 ± 0.16
$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}	E_a/kcal mol^{-1}	log *A*
1.6 ± 1.2	7.3 ± 0.16	13.2 ± 0.26

When the size of R increases (R = Et or Pr^i) the temperature which allows the detection of two separate isomers become lower (−155 and −161 °C respectively): also the intensity of the downfield with respect to the upfield peak increases (Table 2). In the case of (IV) the formyl signal was not split at the lowest attainable temperature; this is consistent with decreasing relative intensity of the less stable rotamer (Table 2) and suggests that in (IV) only one conformation is allowed.

In the aliphatic spectral region of (I)—(III) no splitting of the n.m.r. signals was observed at the lowest attainable temperature. In view of the unambiguous results obtained for the formyl region this can only be explained by a negligible difference in the aliphatic shifts in the two isomers.

The dependence of the isomer ratio on the size of R allowed us to assign the low field formyl signal to the *anti*-isomer and the upfield to the *syn*, because the larger R the smaller is expected to be the relative amount of the more hindered RO-*syn* conformer.* An alternative approach to the conformational assignment of the preferred conformer can be performed by means of ^{13}C n.m.r. spectroscopy. It is well established[8] that in aromatic carbonyl derivatives the more hindered isomers have the ^{13}CO signal shifted downfield with respect to the less hindered analogue owing to the loss of conjugation between the CO group and the aromatic system; this makes the hindered aromatic compounds more similar to the aliphatic carbonyl compounds which have their signal at low fields. In the ^{13}C n.m.r. spectrum (25.15 MHz) the ^{13}CO signal of (I) dissolved in CHF_2Cl is split at −150 °C into two lines 80 Hz apart, the less intense (*ca.* 40%) being downfield with respect to the more intense (*ca.* 60%) peak.† Even allowing for the intensity distortion due to nuclear Overhauser effects there is no doubt that the less intense signal, being downfield, corresponds to the more hindered conformer (*i.e.* RO-*syn*) whereas the upfield is associated with the less hindered species (RO-*anti*).

TABLE 2

Significant parameters for the rotation of the formyl group in benzaldehyde and *ortho*-substituted benzaldehydes (I)—(IV). The $\Delta G^{\ddagger}$ values refer to the forward equilibrium RO-*anti* $\rightleftharpoons$ RO-*syn*; they are the average of all the data obtained from the total line shape method. The isomer ratio is that observed at −160 °C: in the case of (I) this differs from the value obtained at higher temperatures

Compound	*anti* : *syn* Ratio	$\Delta G^{\ddagger}$/ kcal mol^{-1}	$\Delta\nu_{CHO}$ (Hz at 100 MHz)
Benzaldehyde [5]	50 : 50	7.70 ± 0.03	
(I)	64 : 36	6.84 ± 0.02	40.0
(II)	75 : 25	6.42 ± 0.02	41.0
(III)	85 : 15	5.90 ± 0.05	55.0
(IV)	~100 : ~0		

As observed for the isomer ratio the $\Delta G^{\ddagger}$ values also depend upon the size of the substituent: the larger R, the smaller is the free energy of activation.‡ This is consistent with a rotational model involving a planar (or quasiplanar) ground state and a transition state with the CHO plane twisted by $\pi/2$ with respect to the benzene ring. Whereas the twisted transition state is expected to be almost unaffected by the size of R, the ground state will be destabilized when R is varied along the sequence H, Me, Et, Pr^i, Bu^t as steric hindrance will gradually distort the planarity[10] of benzaldehyde, thus reducing

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* Attempts at assigning the conformation of (I) by a nuclear Overhauser experiment failed in that no enhancement of either of the two formyl signals could be detected at −150 °C on irradiation of the methyl signal.

† Although the theoretical explanation is unclear it is worth noting the opposite behaviour of the ^{1}H and ^{13}C signals of the formyl group. The formyl ^{1}H shift of (I) is downfield in the more abundant with respect to the less abundant conformer whereas for the ^{13}C shift the situation is reversed.

‡ In the case of (II) and (III) determination of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ could not be made with reasonable accuracy and therefore is not reported. This is due to the fact that the linewidth measured in the absence of exchange ($\omega = 1/\pi T_2$) cannot be used for measurements taken at higher temperatures owing to the large effects of viscosity near the freezing point of the solvent. Nonetheless the $\Delta G^{\ddagger}$ values are believed to be accurate since these values are much less sensitive to the choice of T_2. This limitation does not apply to (I) since the two isomers can be observed at higher temperatures, where the viscosity effects are negligible. For discussion of this problem see ref. 9.

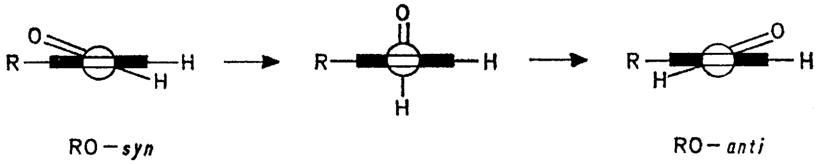
[7] G. Binsch, *J. Amer. Chem. Soc.*, 1975, **91**, 1304; Quantum Chemistry Program Exchange, Indiana University.

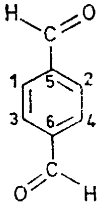
[8] K. S. Dhami and J. B. Stothers, *Tetrahedron Letters*, 1964, 631; *Canad. J. Chem.*, 1964, **43**, 479; J. B. Stothers, '^{13}C N.M.R. Spectroscopy,' Academic Press, New York, 1972; B. F. Bonini, L. Lunazzi, G. Maccagnani, and G. Mazzanti, *J.C.S. Perkin I*, 1973, 2314.

[9] M. Eisenhut, H. L. Mitchell, D. D. Traficant, R. J. Kaufman, J. M. Deutch, and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1974, **96**, 5385.

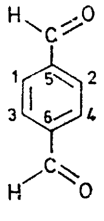
[10] P. Diehl, P. M. Henrichs, and W. Niederberger, *Org. Magnetic Resonance*, 1971, **3**, 243.

the conjugation between CHO and benzene ring. As a consequence the energy difference between the transition and the ground state will decrease in the sequence mentioned.

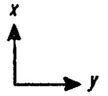




trans



cis



These experiments proved that conformers arising from the restricted motion of CHO can be observed on the time scale of n.m.r. spectroscopy.[11] Accordingly it should also be possible to detect the *cis*- and *trans*-isomers of terephthalaldehyde (V) although at room temperature the four aromatic protons display a single sharp line.

When terephthalaldehyde is electrochemically reduced to the corresponding radical anion the two isomers are detected at room temperature by means of e.s.r., the *trans* being slightly more stable[7] (58%) than the *cis*. Before searching for the same evidence for this phenomenon in the neutral molecule we checked whether the result for the anion is dependent on the way the radical is generated. We therefore generated it by photochemical as well as by chemical reduction. In the first case the radical was obtained by u.v. photolysis of a dimethyl sulphoxide (DMSO) solution of (V) in the presence of potassium t-butoxide.[12] In the second case a solution of (V) in HMPA (hexamethylphosphoric triamide) was allowed to react on a potassium mirror. Both methods yielded radical anions whose e.s.r. patterns were due to the superimposition of two different spectra, of the *trans*- (58%) and of the *cis*-rotamer (42%). Because of the

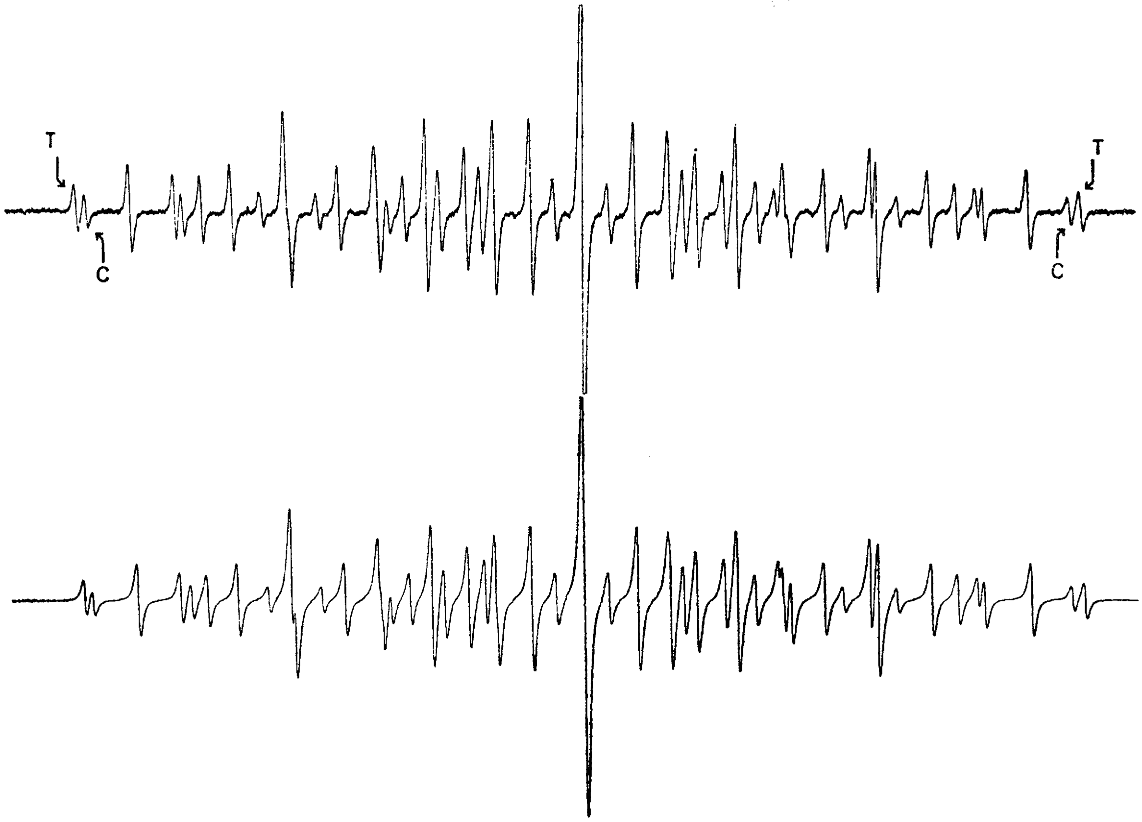


FIGURE 2 Experimental (top) and simulated (bottom) e.s.r. spectrum of terephthalaldehyde radical anion obtained by photolysing a solution of (V) in DMSO containing potassium t-butoxide. The outer lines of the *trans* (58%) and *cis* (42%) isomers are marked with a T and a C respectively. The parameters employed for the simulation are given in Table 3, the linewidth being 0.05 G

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[11] F. A. L. Anet and R. Anet in 'Determination of Organic Structures by Physical Methods,' eds. F. G. Nachod and J. J. Zuckermann, Academic Press, New York, 1971, vol. 3, p. 343.

[12] G. A. Russell in ref. 11, p. 293.

choice of solvents no coupling with the counter-ion was observed, thus indicating that free radicals rather than ion pairs are present. These methods also allowed us to obtain better resolved spectra (line width 0.05 instead of the 0.12 G for the electrochemical reduction): a sample spectrum is shown in Figure 2. Having shown that the existence of the isomers is independent of the ' history ' of the radical anion the phenomenon is thus due to the inherent stability of these two conformers. Even at temperatures as high as 100 °C no *cis-trans*-interconversion is detectable on the e.s.r. time scale, thus confirming that the rotational barriers in the radical anions are larger than in the corresponding neutral molecules.[13] The hyperfine splitting constants of the radical are given in Table 3, the assignment being the same as that of ref. 7.

TABLE 3

Hyperfine splitting constants (G) of terephthalaldehyde radical anions (*cis*- and *trans*-isomers) generated by three different techniques (see text). The assignment is that of ref. 7

	Photochemical (in DMSO)	Chemical (in HMPA)	Electrochemical [7] (in DMSO)
trans (58%)			
H-1, H-4	0.72	0.69	0.70
H-2, H-3	2.06	2.07	2.08
H-5, H-6	3.95	3.69	3.89
cis (42%)			
H-1, H-3	1.54	1.50	1.54
H-2, H-4	1.18	1.20	1.16
H-5, H-6	3.87	3.56	3.81

TABLE 4

Experimental and computed dipolar couplings (Hz) of terephthalaldehyde as obtained from its 100 MHz n.m.r. spectrum in the nematic phase at 78 °C. The experimental data are the output of the LAOCNOR program; the experimental shift difference ($\nu_{CHO} - \nu_{C_6H_4}$) is 234.9 ± 1.7 Hz and the J_H values were taken from ref. 14 ($J_{1.3}$ 7.9, $J_{1.2}$ 1.6, $J_{1.4}$ 0.6 Hz). The computed D_{ij} values were obtained by assuming standard bond lengths and angles: modification of the assumed geometry increased the deviation from experiment. Values in parentheses are absolute deviations

	Experimental	Computed	
		100% *trans*	10% *cis*
$D_{1.2}$	+224.5 ± 1.7	+225.3 (0.9)	+202.9 (21.6)
$D_{1.3}$	−4 594.0 ± 1.2	−4 593.3 (0.7)	−4 605.5 (11.5)
$D_{1.4}$	−34.8 ± 1.3	−38.3 (3.6)	−60.8 (26.1)
$D_{1.5}$	−2 103.4 ± 1.1	−2 100.8 (2.6)	−2 070.7 (32.7)
$D_{3.5}$	−422.1 ± 1.6	−448.8 (26.6)	−444.5 (22.3)
$D_{5.6}$	−205.8 ± 1.7	−187.2 (18.6)	−237.7 (31.9)
R.m.s. deviation		13.4	25.4
$C_{3z^2-r^2}$		−0.510	−0.528
$C_{x^2-y^2}$		0.479	0.471
C_{xy}		−0.017	

Proof that terephthalaldehyde is not a single species in the neutral molecule also is given by its n.m.r. spectrum in the nematic phase (Figure 3). The experimental dipolar couplings (D_{ij}) are not consistent with those computed assuming either only the *cis*- or only the *trans*-conformation (Table 4). Unfortunately only the couplings between the formyl protons $D_{5.6}$ are sensitive to the *trans* : *cis* ratio and therefore the system turns out to be underdetermined for a quantitative study of the relative amount of the conformers.

The final answer to the problem could be only obtained by means of low temperature n.m.r. spectra. When the rotation of the two formyl groups is slowed down on the n.m.r. time scale one would expect in principle that the aromatic protons display, instead of a single line, two AA'BB' spectra (one for the *cis*-, the other for the *trans*-isomer). In the *trans*-conformation however the spectrum should approach an AB type spectrum (four lines) since one coupling ($J_{1.3} = J_{2.4}$) is much larger than the other. On the other hand the $J_{1.3}$ (and $J_{2.4}$) couplings are not detectable in the *cis*-conformer because of the equivalences $\nu_1 = \nu_3$ and $\nu_3 = \nu_4$ and the spectrum should essentially display two lines; owing to the viscosity-broadened linewidth of spectra taken at very low temperature, the whole fine structure is lost. Obviously an accidental coincidence of the chemical shifts of 1- and 2-H would give in both cases spectra formed by a single line. In CHF_2Cl at −153 °C (Figure 4, bottom left) the spectrum of (V) is actually a quartet thus indicating the presence of the *trans*-conformer. However the intensity

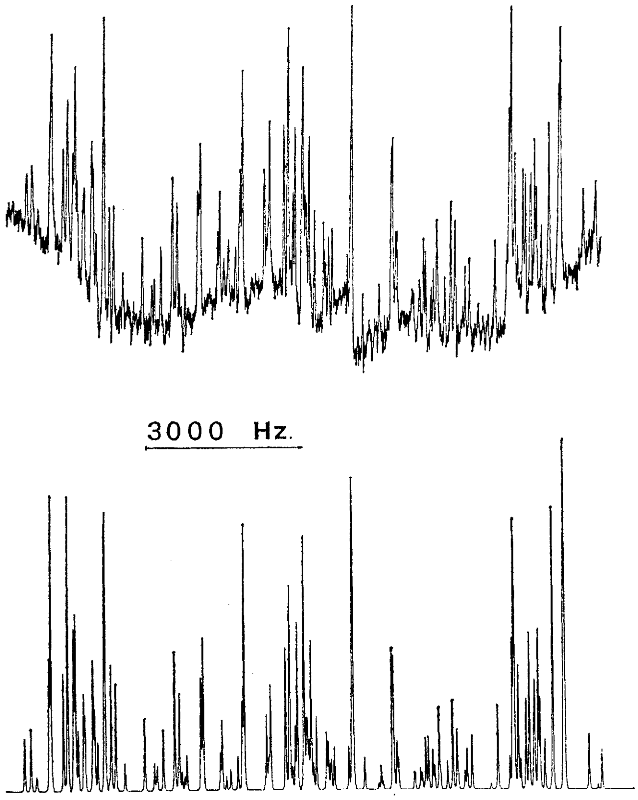

FIGURE 3 Experimental (top) and simulated (bottom) 100 MHz n.m.r. spectrum of (V), partially oriented in the nematic phase of 4,4'-di-n-hexyloxyazoxybenzene at 78 °C. The parameters used for the spectral simulation are given in Table 4. The 85 experimental lines were matched with a r.m.s. deviation of 7 Hz, the average line width being 10.0 Hz

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[13] F. Bernardi, M. Guerra, and G. F. Pedulli, *J. Phys. Chem.*, 1974, **78**, 2144.

of the inner *versus* the outer lines is much higher than expected for an AA'BB' spectrum having the mentioned (see Table 5) J values[14] and the experimentally detectable shifts. Only by assuming that the two lines expected for the *cis*-isomer are superimposed on the inner lines of the *trans* can the experimental ratio be rationalized. In the computer simulation obtained in this way (Figure 4, bottom right) a 1 : 1 ratio of the two conformers was used.

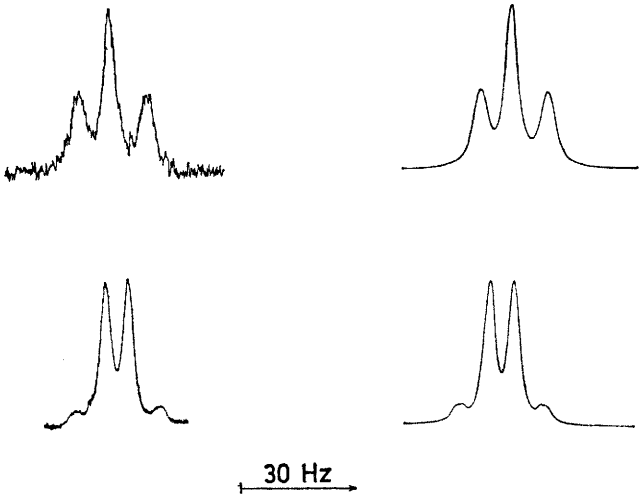

FIGURE 4 Experimental (left) and simulated (right) 100 MHz n.m.r. spectra of the aromatic region of (V) in dimethyl ether (top) at −142 and in CHF_2Cl at −153 °C (bottom)

TABLE 5

Parameters (in Hz at 100 MHz) used for the spectral simulation of terephthalaldehyde (V) at low temperatures (Figure 4). In the case of dimethyl ether as solvent, the centre of the spectrum of the *cis*-isomer is 0.75 Hz downfield from that of the *trans*. For the spectra in CHF_2Cl of the *cis*- and *trans*-isomers the centres of the spectral patterns are coincident. J_{HH} Values were assumed to be equal for both species and were obtained from the data in ref. 14; the *trans* : *cis* ratios are 1.0 (in CHF_2Cl) and 1.08 (in Me_2O)

Solvent	T (°C)	$\Delta\nu_{1.3}$ (*trans*)	$\Delta\nu_{1.2}$ (*cis*)	$J_{1.2}$	$J_{1.3}$	$J_{1.4}$	Linewidth
CHF_2Cl	−153	12.0	6.6	1.6	7.9	0.6	2.7
$(CH_3)_2O$	−142	5.6	17.5	1.6	7.9	0.6	3.3

On the other hand in dimethyl ether the single line spectrum of the aromatic protons of (V) is split, at −142 °C, into an asymmetric triplet (Figure 4, top left). The outer lines which have a 1 : 1 ratio undoubtedly belong to the spectrum of the *cis*-rotamer whereas the central line can be interpreted as due to the *trans*-rotamer having the 1- and 2-H shifts almost coincident within the experimental linewidth (*ca.* 3 Hz). A satisfactory computer simulation (which again employed the J_{HH} values of ref. 14) was obtained using a *trans* : *cis* ratio of 52 : 48 (Figure 4, top right). The chemical shift differences employed in the computer simulation are quoted in Table 5.[*]

We may thus conclude that evidence as clear as that given for *ortho*-substituted benzaldehydes has been obtained for the existence of two rotamers of terephthalaldehyde. The *trans* : *cis*-ratio of *ca.* 1 : 1 indicates that the two formyl groups rotate independently; in the radical anion, on the other hand, the conjugation pathway of the *trans* is slightly more favoured than that of the *cis*-rotamer. The difference between the *trans* : *cis*-ratio however is small enough to confirm[15] that the conformational preference of the radical anion can be considered, in many respects, equal to that of the neutral species.

EXPERIMENTAL

Spectral Measurements.—Spectra of ^{13}C *o*-methylbenzaldehyde were obtained in the Fourier transform mode at 25.15 MHz with proton noise decoupling. Samples were prepared by placing in 10 mm tubes the compound under examination, the reference (tetramethylsilane), and some $(CD_3)_2CO$ which is needed for the heteronuclear locking system. The tubes were then connected to a vacuum line and the solvent (CHF_2Cl) was condensed into the tube using a liquid nitrogen bath. The tubes were then sealed off under vacuum and allowed to reach room temperature: ordinary n.m.r. tubes were able to sustain the pressure. *ca.* 500 Pulses at 75° with a repetition time of 1.5 s were used to record the ^{13}C spectra at *ca.* −150 °C.

^1H N.m.r. spectra were recorded at 100 MHz in the continuous wave mode with 5 mm tubes using internal lock on tetramethylsilane or external lock on H. For the variable temperature measurements a dummy sample containing a thermocouple was placed in the probe after each recording. The sequence was repeated many times by increasing and decreasing the temperature to reduce random errors; nevertheless uncertainty in the temperature <0.5° could not be reached.

The liquid crystal spectra were run in 4,4'-n-hexyloxyazoxybenzene at 78 °C. Owing to the low solubility of terephthalaldehyde no spectra due to oriented molecules could be detected using as solvents substances which are nematic at room temperature. As a consequence the better stability that can be obtained using room temperature nematogens is lost and the relatively large experimental errors may be due to slight temperature fluctuation inside the probe.

E.s.r. spectra were recorded by placing in the microwave cavity of the spectrometer a capillary tube (1 mm diam.) containing terephthalaldehyde dissolved in DMSO with a small amount of potassium t-butoxide: on photolysis with a Xenon lamp the spectrum is obtained at room or higher temperatures (Figure 2). The spectrum disappears when irradiation is stopped. Alternatively the radical was

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[*] No attempt was made to evaluate the $\Delta G^\ddagger$ value since too many needed parameters [such as $J_{HH}(cis)$ and $J_{HH}(trans)$, T_2, and chemical shift differences] could not be obtained with sufficient accuracy.

[14] S. Castellano, *J. Amer. Chem. Soc.*, 1966, **88**, 4741; *Tetrahedron Letters*, 1967, 4635, 5205, 5211; K. Hayamizu and O. Yamamoto, *J. Mol. Spectroscopy*, 1969, **29**, 183; 1968, **25**, 422.

[15] L. Lunazzi, G. F. Pedulli, M. Tiecco, and C. A. Veracini, *J.C.S. Perkin II*, 1972, 751, 755.

obtained[16] by placing a solution of (V) in HMPA into the longer arm of a T shaped tube. The solution was degassed and a potassium mirror prepared under high vacuum in the shorter arm. This system was then sealed under vacuum and the solution allowed to react with potassium; the radical produced in this way is stable for a few hours.

Preparation of Compounds.—Derivatives (I) and (V) were commercial and were purified before use.

o-Alkylbenzaldehydes (II)—(IV) were prepared[17] from the corresponding *o*-alkylbromobenzenes by reaction with lithium. The aryl-lithium intermediate was then allowed to react with *NN*-dimethylformamide and the reaction mixture treated with aqueous ammonium chloride. The reaction details are the same as those reported in ref. 17 for aliphatic aldehydes. The products (II)—(IV) were then purified by treatment with potassium hydrogen sulphite followed by distillation under reduced pressure. The b.p.s agree with those in the literature[18] and the n.m.r. spectra are as expected.

The *o*-alkylbromobenzenes were prepared[18] from the corresponding 4-nitroalkylbenzenes by treatment with bromine in H_2SO_4 in the presence of Ag_2SO_4. The nitro-group was then cleaved by reducing it to amino followed by diazotisation and treatment with hypophosphorous acid.

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[16] L. Lunazzi, G. Placcucci, and R. Danieli, *J. Amer. Chem. Soc.*, 1971, **93**, 5850.

[17] E. A. E. Evans, *J. Chem. Soc.*, 1956, 4691.

[18] M. H. Klouwen and H. Boelens, *Rec. Trav. chim.*, 1960, **79**, 1022.