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^{13}C NMR and Force Field Calculations on the Barrier to Internal Rotation in and Conformational Equilibria of the Benzenedicarbaldehydes

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The proton coupled ^{13}C NMR spectra of the three benzenedicarbaldehydes have been fully analysed. The barrier to internal rotation of the formyl groups has been obtained from band-shape analysis of the low temperature proton noise-decoupled ^{13}C spectra, resulting in $\Delta G^{\ddagger}$ values of 31.0 ± 0.5 and 28.6 ± 0.5 kJ/mol for 1,3- and 1,4-benzenedicarbaldehyde, respectively. At the lowest temperatures (*ca.* -150 °C) the rotamer equilibria for these two isomers could also be determined. This was not possible for 1,2-benzenedicarbaldehyde where either predominantly one conformation is adopted or the barrier to rotation is lower than for the other compounds. Force field calculations indicate a barrier to internal rotation considerably lower for the 1,2 isomer than for the other two.

In previous work we have determined the formyl rotational barrier in some *para*-substituted benzaldehydes [1a] and both the barrier and conformational equilibria for some *ortho*- and *meta*-substituted benzaldehydes.[1b] As a continuation we have now also studied the three different benzenedicarbaldehyde isomers.*** In the present work the proton coupled carbon-13 spectra have also been studied to find out if the magnitude of the $^{13}C-^{1}H$ coupling constants can be useful in estimations of conformational equilibria, in the same way as the proton-proton five-bond coupling has been used.[3] We also report some force field calculations on these compounds,[4] which have been performed in order to confirm the conclusions drawn regarding especially the barrier in the 1,2 isomer.

RESULTS AND DISCUSSION

^{13}C NMR spectra. Carbon-13 spectra have been obtained from 0.5 M Freon solutions at low temperature as well as from concentrated chloroform solutions to determine the $^{13}C-^{1}H$ spin coupling constants. For 1,4-benzenedicarbaldehyde the assignment is obvious as there is only one aromatic carbon signal from four equivalent proton-bearing carbons and one from two non-proton-bearing carbons. For 1,3-benzenedicarbaldehyde the assignment of the aromatic ^{13}C resonances was made from the behaviour of the signals at low temperature. This assignment is also in agreement with the expected spin coupling pattern of the various resonances. The 1,2-benzenedicarbaldehyde spectrum showed no temperature dependence and the assignment is thus based on the coupling pattern only. The substituent induced shifts are not used as they are known to be less accurate for *ortho*-substituted benzenes and furthermore the unknown conformation equilibrium makes them even less usable.[1a] The observed chemical shifts are summerized in Table 1. All the $^{13}C-^{1}H$ coupling constants have been

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[***] It has recently been shown by Lunazzi *et al.* that the torsional barrier in the 1,4 isomer is sufficiently high to be observed by NMR.[2] The activation energy was, however, not determined.

Table 1. Carbon-13 chemical shifts of the benzenedicarbaldehydes in Freon solution at −70 °C. Shift in ppm downfield from TMS.

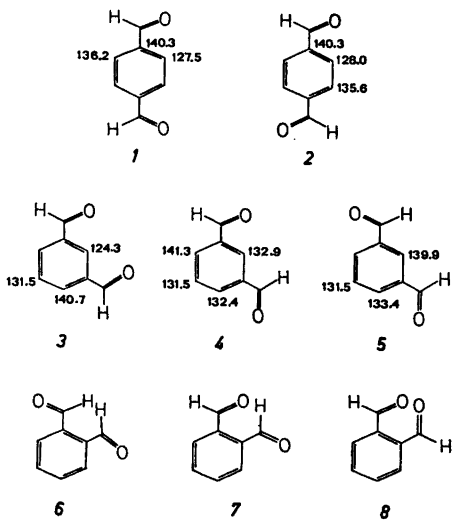
Isomer	C-1	C-2	C-3	C-4	C-5	C-6	CHO
1,2	137.2	137.2	133.1	135.8	135.8	133.1	196.1
1,3	137.9	132.6	137.9	136.4	131.5	136.4	193.8
1,4	141.2	131.7	131.7	141.2	131.7	131.7	201.9

Table 2. $^{13}C-^{1}H$ spin coupling constants in the three benzenedicarbaldehydes.

	H-2	H-3	H-4	H-5	H-6	H-7	H-8
1,2-Isomer							
C-1		6.43	−1.07	6.93	0.38	24.85	1.91
C-3		163.03	1.61	7.71	−0.89	0.51	2.10
C-4		0.85	163.83	1.47	7.55	0.00	0.41
1,3-Isomer							
C-1	0.35		−0.58	7.14	0.44	24.94	0.74
C-2	162.85		6.54	−1.37	6.54	2.00	2.00
C-4	6.34		162.75	1.79	7.81	0.00	1.99
C-5	−0.49		0.70	165.11	0.70	0.49	0.49
1,4-Isomer							
C-1	–[a]	–[a]		–[a]	–[a]	24.70	0.00
C-2	163.4	0.97		−1.96	7.16	1.97	0.45

[a] Not determined.

determined from the proton coupled ^{13}C spectra. It was not possible to make a first order analysis since the proton spectra are strongly coupled and thus the computer program UEAITR[5] was used to simulate the ^{13}C spectra. The obtained coupling constants are given in Table 2 and in Fig. 1 the aromatic part of the proton coupled spectrum from 1,2-benzenedicarbaldehyde is shown. As can be seen there is an overlap between the downfield parts of the C-1, C-2 and C-4, C-5 resonances making the analysis of the C-1, C-2 spectrum difficult. In order to get a clear spectrum from the C-1, C-2 carbons we used the $180-\tau-90$ pulse sequence with τ adjusted to get a null signal from the C-4, C-5 resonance, resulting in the spectrum shown in Fig. 2. This procedure worked very well in this case where there was a large difference in the spin-lattice relaxation time for the C-1, C-2 and C-4, C-5 resonances. Our results on the coupling



Scheme 1.

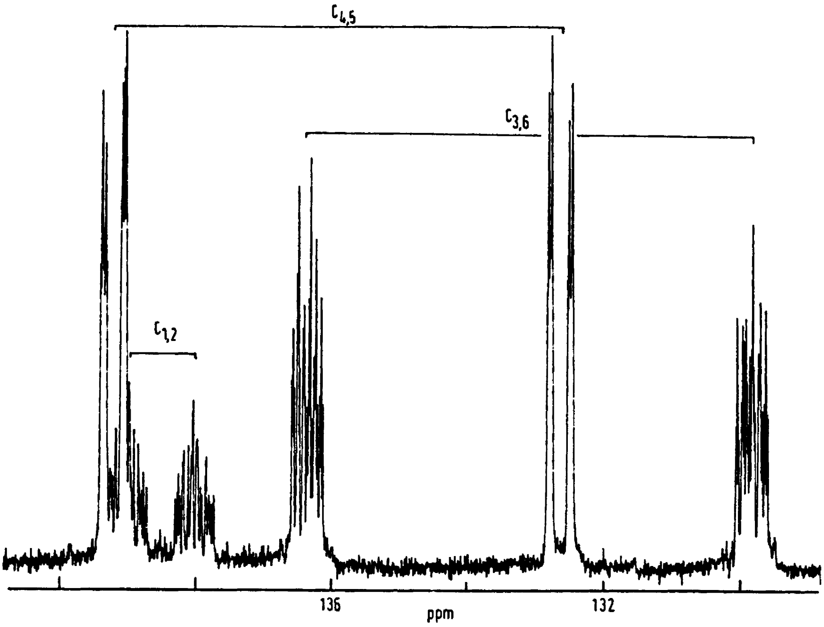


Fig. 1. ^{13}C proton coupled NMR spectrum of the aromatic carbons in 1,2-benzenedicarbaldehyde.

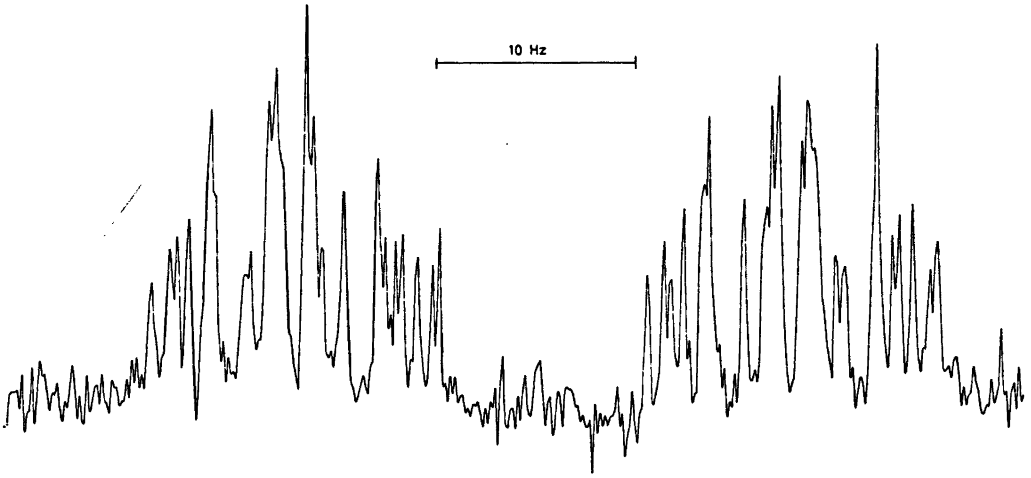


Fig. 2. An expansion of the C-1 resonance in 1,2-benzenedicarbaldehyde, obtained without proton decoupling. The $(T-180-\tau-90)_n$ pulse sequence was used with $T=30$ s and $\tau=3.1$ s to null the signals from the C-4 and C-5 carbons.

constants are in fair agreement with previous fragmentary data.[6,7]

In Scheme 1 the planar or nearly planar conformers of the benzenedicarbaldehydes are shown together with the assignment of the carbon-13 resonances to the various conformers for 1,3 and 1,4 isomers. The shifts for the 1,3 isomer were obtained at −141 °C and those for the 1,4 isomer at −160 °C. The effect from the orientation of the formyl group on the shift of the *meta* carbons is not well-known, but a comparison with *m*-fluorobenzaldehyde in-

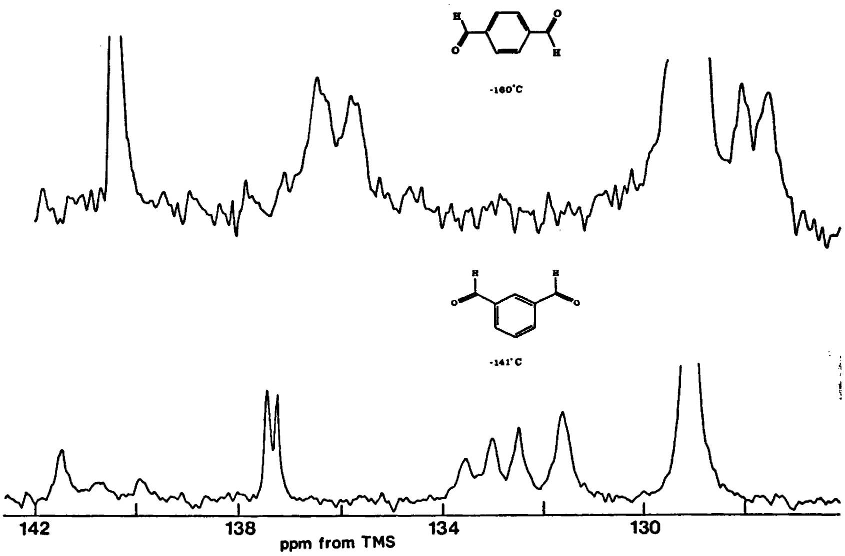


Fig. 3. Parts of the low temperature proton noise-decoupled ^{13}C NMR spectra from 1,3- and 1,4-benzenedicarbaldehyde.

dicates that the assignment should be as given for 1,4-dicarbaldehyde. For the 1,3 isomer a more reliable assignment could be made due to the non-equal populations of the various rotamers, see Fig. 3. For two pairs of signals the assignment is only tentative, the favoured one is, however, the one that is in best agreement with the high temperature chemical shifts (−70 °C). In principle it should be possible to make a complete assignment of the signals in the 1,3 isomer from a bandshape analysis of the spectrum in the temperature region where the shape is temperature dependent due to exchange. This was, however, not possible since the quality of the spectra was not sufficiently high (Fig. 3).

Conformational equilibria. At low temperature where the rotation about the formyl bond is slow on the NMR time scale the population of the various rotamers can be directly obtained from the spectrum. For 1,4-benzenedicarbaldehyde the high temperature signal from the four equivalent carbons gives rise at low temperatures to four signals of almost identical intensity, showing that the populations of the two rotamers are approximately equal. This means that the orientation of a *p*-formyl group has no influence on the orientation of the other formyl group. This is also confirmed by force field calculations, which gave the same energy for the two rotamers when the dipolar energy was neglected. The calculated difference in the dipolar energy for the two planar rotamers, *1* and *2*, was *ca.* 1.2 kJ/mol for an isolated molecule. Since the dipolar energy [8] is strongly dependent on the "effective" dielectric constant, the dipole-dipole interaction should be negligible. (The Freon dielectric constant is estimated to be *ca.* 10 at the temperature in question). Barassin *et al.*[9] have reported the same 50:50 population ratio based on dipole moment measurements, whereas Gore *et al.*[10] suggest that the molecule cannot be planar since their dipole moment and Kerr constant are not in agreement with a mixture of two planar conformations. An SCF-MO calculation,[11] however, also indicates that 1,4-benzenedicarbaldehyde should exist as a 50:50 mixture of the two planar conformations.

The force field calculations on the 1,3 isomer indicate that all three different rotamers (all planar) should be present in solution, with about the same populations (Table 3). As can be seen from Fig. 3 a fairly complicated ^{13}C NMR spectrum was obtained in the aromatic region at low temperature. The assignment

Table 3. Relative energies of the various rotamers as obtained from the force field calculations.

Rotamer[a]	E kJ/mol	E' kJ/mol[b]
1	0.0	20.2
2	0.0	20.2
3	0.0	20.2
4	0.0	20.2
5	0.0	20.2
6	0.0	13.0
7	1.1	13.0
8	7.1	–

[a] See Scheme 1. [b] Energy obtained when the formyl group on C-1 is perpendicular to the benzene ring. The calculated [4] and experimental [12] barrier for benzaldehyde is 20.5 kJ/mol in the gas phase. The gas phase numbers may be corrected for solvation by adding *ca.* 10 kJ/mol, which is the difference in rotational barrier between gas phase and solution.

was, however, straightforward as discussed above and the populations were obtained from the spectrum at −141 °C by means of a total bandshape analysis treating the spectrum as two overlapping four-site cases resulting in the population 0.15, 0.58 and 0.27 for rotamers *3*, *4* and *5*, respectively. The corresponding energy difference between rotamers *3* and *4* is 0.7 kJ/mol with an accuracy of *ca.* ± 0.03 estimated from the agreement between experimental and calculated bandshapes. Observe that the *4* isomers are two identical ones, which have been taken into account when calculating the energy difference. These results are in reasonable agreement with previous dipole moment [9] and theoretical data.[11]

As discussed above the ^{13}C NMR spectrum of the 1,2 isomer showed no pronounced temperature dependence. There are two possible explanations to this behaviour, either the rotation of the formyl groups is sufficiently fast, even at the lowest temperatures, to make the observation of signals from individual rotamers impossible and/or the molecule is predominantly in conformer *6* or *8*. (Rotamer *7* should under slow exchange conditions give rise to a more complex spectrum since the C-3 and C-6 carbons are not equivalent.) From measurements on other *ortho*-substituted benzaldehydes [1b] we have observed that they are normally in the *trans* conformation. For *ortho*-Me, however, the population ratio is 50:50 and the barrier is reduced but not below the level of detectability. The force field calculations rule out rotamer *8* as the dominant one, whereas the other two, *6* and *7*, might be present in comparable amounts, (Table 3), which is also indicated by the magnitude of the proton-proton five bond coupling to the aldehyde protons, $J = 0.3$ Hz, and the published dipole moment.[9] The force field calculations also indicate that the formyl groups in the two low energy conformers, *6* and *7*, are twisted 10 to 20° out of the ring plane and the barrier is reduced *ca.* 7 kJ/mol, compared to the other two diformylbenzenes (Table 3). It thus seems probable that the fact that we cannot observe any effect from slow rotation on the ^{13}C spectrum in 1,2-benzenedicarbaldehyde is due to a low torsional barrier, *ca.* 20 kJ/mol.

When we initiated this work we decided to determine all $^{13}\mathrm{C}-{}^{1}\mathrm{H}$ coupling constants to investigate the possibility of using them to estimate the orientation of the formyl groups. We found that the three-bond coupling to the formyl proton is *ca.* 2 Hz and the four-bond one *ca.* 0.5 Hz and that these do not change in a systematic way with the conformation of the formyl group. These molecules are, however, not very well suited for this investigation. Both the 1,3 and 1,4 isomers have population ratios close to 50:50 and the 1,2 isomer is probably not planar. None of the coupling constants seem to be as sensitive to the formyl group orientation as the $^{1}\mathrm{H}-{}^{1}\mathrm{H}$ five-bond coupling. For a series of *p*-substituted benzaldehydes, however, we found that the magnitude of the two-bond coupling to the formyl proton varies linearly with the free activation energy of the formyl rotation barrier, as shown in Fig. 4.

Torsional barriers. For both the 1,3- and 1,4-dicarbaldehydes the barrier to internal rotation was determined from band shape analysis of low temperature ^{13}C NMR spectra. In these cases each of the signals, equivalent at high temperature, can in principle give rise to three or four different signals at low temperature due to the effect of the "frozen-out" rotation of two formyl groups. The high temperature singlet from the 2-, 3-, 5- and 6-carbons for the 1,4 isomer is split into four signals of almost equal intensity at temperatures below −140 °C

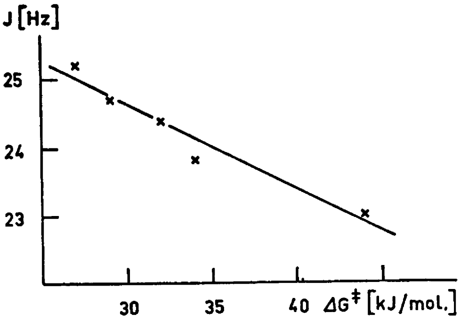


Fig. 4. A plot of the magnitude of the two-bond proton – carbon-13 coupling (C-1 – aldehyde proton) against the activation free energy for the formyl group rotation.

and as can be seen from Fig. 3 the low temperature spectrum from the 1,3 isomer is fairly complex, but is easily interpretable. The signals from the aldehyde carbon and the ring carbons 1 and 3 are little influenced by the orientation of the formyl groups and give rise to narrow doublets. The 2-carbon can give rise to three different signals and the 4- and 6-carbons can give four signals. All these signals are really observed at low temperature (below $-135\,°C$). The remaining signal at 131.7 ppm is from the 5-carbon and never splits but broadens slightly at the lowest temperature. This could in principle be a triplet.

In order to calculate the exchange rates from these spectra it was necessary to treat them as four site exchange cases, and furthermore the 1,3 isomer was treated as two overlapping four site exchange cases. For the 1,4 isomer the band-shape calculations were made on spectra from -108 to $-143\,°C$ resulting in $\Delta G^{\ddagger} = 28.6 \pm 0.5$ kJ/mol and for the 1,3 isomer from -98 to $-127\,°C$ resulting in $\Delta G^{\ddagger} = 31.0 \pm 0.5$ kJ/mol. For both the compounds $\Delta S^{\ddagger}$ was found to be close to zero and slightly negative ($|\Delta S^{\ddagger}| < 10$ J/mol) in agreement with other formyl group torsional barriers.[1a] The free energy of activation data are also in good agreement with the data for other benzaldehydes and also demonstrate a stronger effect from a *p*-substituent as compared to an *m*-substituent. The force field calculations, however, gave the same activation energy for both the 1,3 and 1,4 isomers.

EXPERIMENTAL

The benzenedicarbaldehydes were commercial products from FLUKA AG (Switzerland) and were recrystallized before use. The Freons were from Hoechst AG (Germany) and were used without purification.

The low temperature spectra were obtained as described before[1b] and to obtain proton coupled spectra the gated decoupling technique was used to retain the Overhauser effect and in one case a $180 - \tau - 90$ pulse sequence was used to nullify the signals from the proton-bearing carbons and in this way isolate the spectrum from the substituted ring carbons. In this latter case we used a pulse delay of 30 s and $\tau = 3.1$ s.

The calculation of the bandshapes of the low temperature spectra were made by means of a four-site exchange program, described elsewhere[13] with the exchange between single lines. For the 1,3 isomer the final bandshape was the sum of two independent four-site cases. The determination of the rate constants was made by means of a visual fitting of the calculated to experimental spectra, which always gave excellent agreement. All calculations were performed on a Univac 1108 computer.

The temperature in the sample was measured with a thermocouple fixed inside the insert as described previously.[1b]

The force field calculations were performed as described by Liljefors and Allinger.[4]

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