Conformational Studies by Dynamic NMR. 62.[1] Stereomutations of Rotamers and of Conformational Enantiomers in 1,2-Diacylbenzenes

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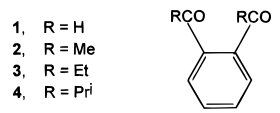
A number of 1,2-diacylbenzenes have been investigated by dynamic NMR spectroscopy. The 1,2-formyl derivative **1** was found to exist (at −162 °C) in the nearly coplanar *ZE* and *EE* conformations (70% and 30%, respectively) that interconvert with a free energy of activation of 4.9 kcal mol^{-1}. On the contrary, the more hindered 1,2-diisobutanoylbenzene (**4**) adopts a twisted conformation (as indicated by the ^{13}C spectrum at −157 °C) which, in principle, might correspond either to a *meso* or to a racemic stereolabile structure. Only the racemic conformer is, however, believed to be populated, and the interconversion barrier between the *RR* and *SS* conformational enantiomers has been determined (5.6 kcal mol^{-1}). Although the 1,2-diacetyl- and 1,2-dipropanoylbenzenes did not exhibit dynamic NMR effects in solution, they were assigned a twisted (racemic) conformation on the basis of the corresponding solid state ^{13}C CP-MAS spectra, in that they display a 1:1 doublet signal for each pair of enantiotopic carbons. All these conclusions agree with the predictions of molecular mechanics calculations.

Introduction

Whereas benzaldehydes, even when *ortho*-substituted, maintain an essentially planar conformation,[3] *ortho*-substituted diaryl or alkyl aryl ketones adopt twisted conformations, with the Ar−CO dihedral angle in the range 45−90°.[3] The latter situation can be directly detected in solution by monitoring, usually at low temperature, the anisochronous NMR signals due to diastereotopic groups of appropriate prochiral substituents.[4−9] The free energy of activation ($\Delta G^{\ddagger}$) for the Ar−CO rotational process can be determined by computer simulation of the temperature dependent line shape of these NMR signals. If the *ortho* substituents are such as to eliminate the plane of symmetry, two conformational enantiomers are created at low temperature, by virtue of the Ar−CHO chirality axis. These enantiomers can be, in principle, observed by recording the low-temperature NMR spectra in a chiral environment.[7,10]

As a consequence, if the molecule comprises a pair of equal carbonyl substituents, the presence of two identical chirality axes gives rise to a *meso* and to a racemic conformer in unequal proportions.[7,8,11] The assignment of their structure, however, cannot be easily achieved in solution since both such conformers display the same spectral multiplicity.[12,13]

Although 1,2-diacylbenzenes represent the simplest example of the situation described above, they have not been so far investigated for this purpose. In the present work we approached this problem by applying the dynamic NMR method to the following derivatives, each of them bearing two equal carbonyl moieties at positions 1 and 2 of the benzene ring.



Results and Discussion

As previously mentioned, 1,2-diformylbenzene **1** (R = H), contrary to ketones **2**−**4**, is expected to be planar or quasi-planar (i.e., with an Ar−CHO dihedral angle not larger than 45°).[3] Actually a number of *ortho*-substituted benzaldehydes were found to display, at appropriate low temperatures, NMR spectra due to unequally populated *E* and *Z* conformers[14] which, to be observed, require the existence of a plane of symmetry coincident with that of the benzene ring.[15]

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(2) In partial fulfillment of the Ph.D. requirements in Chemical Sciences, University of Bologna.

(3) (a) Abraham, R. J.; Angiolini, S.; Edgar, M.; Sancassan, F. *J. Chem. Soc. Perkin Trans. 2* **1995**, 1973. (b) Abraham, R. J.; Angiolini, S.; Edgar, M.; Sancassan, F. *J. Chem. Soc. Perkin Trans. 2* **1997**, 41 and references cited therein.

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(11) Staab, H. A.; Chi, C.-S.; Dabrowski, J. *Tetrahedron* **1982**, *38*, 3499.

(12) Casarini, D.; Lunazzi, L.; Foresti, E.; Macciantelli, D. *J. Org. Chem.* **1994**, *59*, 4637.

(13) When the compound is solid, X-ray diffraction provides an unambiguous answer on the assumption, however, that the structure of the conformer in solution is the same as in the crystal.

(14) (a) Drakenberg, T.; Jost, R.; Sommer, J. M. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1682. (b) Lunazzi, L.; Ticca, A.; Macciantelli, D.; Spunta, G. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1121.

(15) Either the CHO group is actually coplanar with the benzene ring or it librates by a small angle (lower than 45°) above and below the aromatic plane, with such a low barrier as to create, in practice, a dynamic plane of symmetry.

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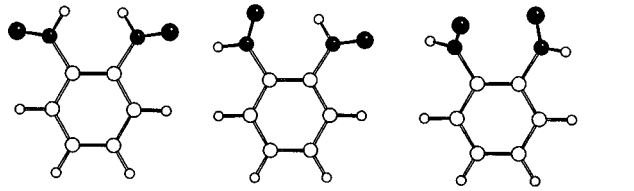
Scheme 1. MM-Computed Structures of the Three Conformers of 1 (the C=O Bonds are Represented as Black)[a]



1-EE (E = 0.95) **1**-ZE (E = 0) **1**-ZZ (E = 1.15)

[a] The computed energy values (E) are given in kcal mol^{-1}.

In the particular case of **1**, therefore, we expect three planar (or quasi-planar) conformers, corresponding to the three energy minima of the molecular mechanics (MM) calculations[16] displayed in Scheme 1, where the relative energies (E) are expressed in kcal mol^{-1}. Previous calculations[17] had indicated the symmetric conformer **1**-EE as the most stable of the three, and low-temperature NMR ^{13}C spectra of **1** had not shown any modification of the spectral multiplicity. If a symmetric conformer such as **1**-EE is indeed the only populated conformer, the NMR spectrum would display the same number of lines both in the case of fast and slow rotation, thus making the dynamic process invisible to NMR. Consequently, the failure of detecting modifications of the spectral multiplicity was, apparently, in agreement with such a theoretical prediction.[17]

As it appears in Scheme 1 our MM approach[16] predicts, on the contrary, that the unsymmetric conformer **1**-ZE should be the most stable, a conclusion that would allow NMR detection of line splittings, if the Ar−CHO rotation is rendered sufficiently slow.

Indeed, as shown in Figure 1, the ^{1}H line of the aldehydic protons of **1** splits at −162 °C. At the same temperature also one of the ^{13}C lines of the aromatic CH carbons broadens much more than the other, reaching the coalescence point; the poor signal-to-noise ratio (due to the poor solubility at such a low temperature) makes, however, this spectrum less informative.

The computer simulation of the ^{1}H aldehydic signal reported on the top of the experimental spectrum of Figure 1 is the result of the superimposition of a single line (30%) upon one of a pair of equally intense lines (35% each), all of them experiencing the effect of an exchange process. This requires the existence of a symmetric and of an unsymmetric conformer in a 30:70 ratio, the pair of equally intense lines being obviously due to **1**-ZE.[18] The chemical shift separation of these two lines (about 0.58 ppm) is in keeping with the separation observed in a similar situation for other *ortho*-substituted benzaldehydes (0.4−0.55 ppm).[14b] The more deshielded of this pair of lines should correspond to the HCO hydrogen in a *syn* relationship to the second HCO substituent, by analogy with other *ortho*-substituted benzaldeydes reported in the literature.[14b] Since the single line of the minor symmetric conformer is almost superimposed to the more deshielded line of **1**-ZE, it is conceivable to assign it to conformer **1**-EE. For, in this conformer each HCO hydrogen is likewise *syn* to the second HCO substituent. Such an assignment also agrees with the MM results (Scheme 1) that indicate conformer **1**-EE to be less stable than **1**-ZE but slightly more stable than **1**-ZZ.[19]

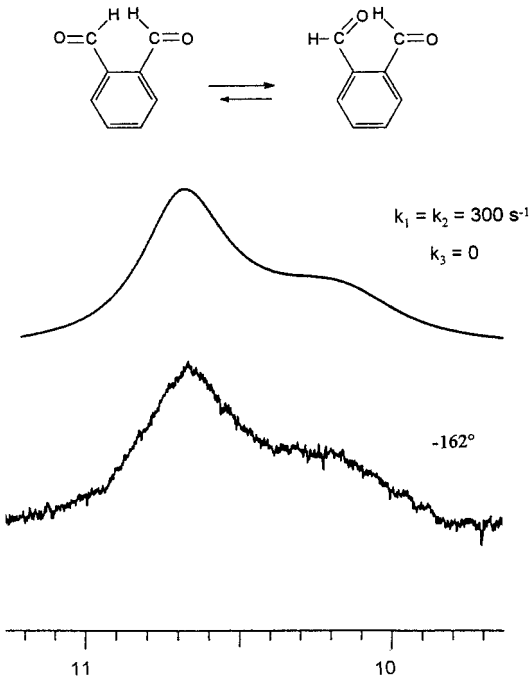


Figure 1. ^{1}H signal (300 MHz in CHF_2Cl) of the aldehydic hydrogen of **1** at −162° C (bottom). On the top is reported the computer simulation obtained with the rate constants indicated (see text).

The line shape simulation of Figure 1 has been achieved by using rate constants that exchange the single line of conformer **1**-EE with each of the two lines of **1**-ZE (k_1 and k_2, respectively). The rate constant (k_3) for a direct exchange between the two lines of **1**-ZE was considered negligible. This model is the consequence of the following considerations concerning the interconversion mechanism. It is in fact conceivable that rotation of the CHO group bonded to C-1 in **1**-ZE generates conformer **1**-EE and that a subsequent rotation of the CHO group bonded to C-2 in **1**-EE generates back **1**-EZ (identical to **1**-ZE) and *vice versa*.[20] Thus each line of the unsymmetric conformer exchanges with the line of the symmetric one with the same rate (thus $k_1 = k_2$). On the other hand it is extremely unlikely that *both* the formyl groups of **1**-ZE rotate *simultaneously* to yield **1**-EZ: this is the reason for having neglected the rate constant for the direct interconversion (*viz.* $k_3 = 0$ in Figure 1). The same type of mechanism was demonstrated to hold in a similar situation, albeit in a different molecule.[21] On this basis[22] the experimental free energy of activation ($\Delta G^{\ddagger}$) for the interconversion process of **1**

(16) Use was made of the programs GMMX (for searching the conformational minima) and PC MODEL (employing the MMX force field), as implemented by Serena Software, Bloomington, IN.

(17) Bernassau, J.-M.; Drakenberg, T.; Liljefors, T. *Acta Chem. Scand.* **1977**, *B31*, 836.

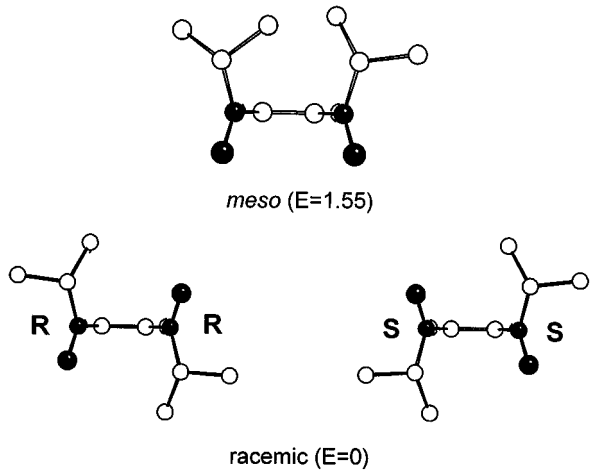
(18) This interpretation received further support from the ^{13}C spectrum of **1** obtained in the solid state, where the most stable among the possible conformers is, usually, the only observed species. The signal of the proton decoupled HCO carbons is in fact a 1:1 doublet ($\Delta\nu$ = 1.8 ppm), as expected for the unsymmetric ZE conformation of Scheme 1 (the ring carbon signals overlap too much to be meaningfully interpreted).

(19) In principle, it cannot be excluded that, underneath the more intense signals, there is also the single line of the third (symmetric) **1**-ZZ conformer, albeit in a quite small proportion.

(20) Of course the same CHO bonded to C-1 can rotate back, with equal probability, yielding again **1**-ZE.

(21) Anderson, J. E. ; Casarini, D.; Lunazzi, L. *J. Org. Chem.* **1996**, *61*, 1290.

Scheme 2. MM-Computed Structures (Top View) of the *Meso* and Racemic Conformers of 4 (the C=O Bonds Are Represented as Black)[a]



[a] The computed energy values (E) are given in kcal mol^{-1}.

turns out to be 4.9 ± 0.3 kcal mol^{-1}, a value quite lower than those measured for its less hindered 1,3 and 1,4 structural isomers (7.4 and 6.8 kcal mol^{-1}, respectively,[17] for 1,3- and for 1,4-diformylbenzene). Such a low value is a consequence of the reciprocal steric effect of the *ortho* formyl substituents that make the ground states of **1** less stable[14b] than those of the two mentioned isomers, whereas the orthogonal transition state of **1** is, obviously, much less affected by the *ortho* substitution. Our MM calculations indicate, in fact, that the Ar−CO dihedral angles are in the range 20−30° in **1**-ZE and **1**-EE,[23] whereas they are essentially 0° in 1,3- and in 1,4-diformylbenzene; the latter ground states are thus stabilized, with respect to **1**, owing to a more efficient conjugation.

The MM calculations for ketones **2**−**4** yield only two, rather than three, energy minima:[16] this is because they adopt twisted conformations (the computed Ar−CO dihedral angles are about 60°) that entail, as mentioned, a *meso* and a racemic diastereomeric conformer (an example is shown in Scheme 2 for R = Pr^i, (**4**) where the relative energies, E, are in kcal mol^{-1}).

Low-temperature NMR spectra of **2** did not show any line splitting, nor line broadening attributable to a dynamic process. Since **2** does not have any prochiral substituent, the negative result implies either that only one diastereomeric conformer is populated or that the rotational barrier is too low to produce noticeable spectral changes. It is also quite possible that both situations apply. Likewise we failed to detect a dynamic process in **3** (R = Et). Here, however, the ^{1}H spectrum would display anisochronous CH_2 signals if the Ar−CO rotation was slow in the NMR time scale, even in the case that only one of the two conformers (*meso* or racemic) was populated. As a consequence the negative result is undoubtedly due to a barrier too low to be observed in our experimental conditions.

On the contrary, in the ^{13}C spectrum of **4** (R = Pr^i) the methyl peak splits into a 1:1 doublet below −146 °C

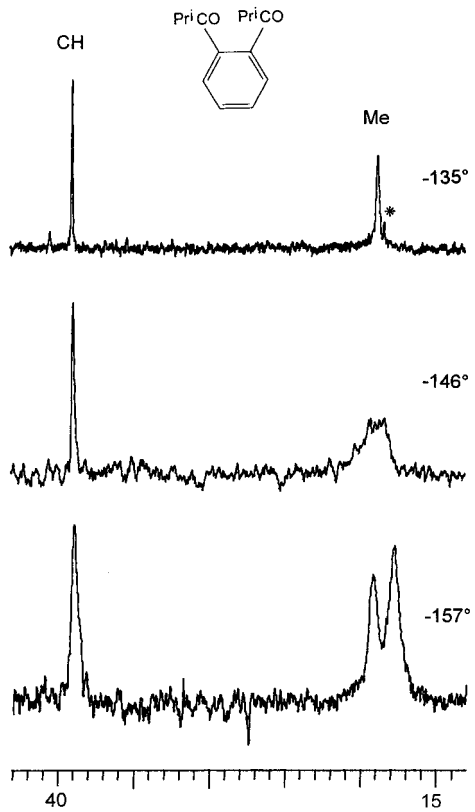


Figure 2. ^{13}C spectrum (100.6 MHz in CHF_2Cl) of the isopropyl group of **4** as a function of temperature. The asterisk indicates an impurity.

(Figure 2) whereas all the other peaks remain unsplit (the more shielded Me peak appears slightly more intense than its deshielded companion since an impurity, clearly visible also in the −135 °C spectrum, has a similar shift). This experiment proves that, being the Ar−CO rotation frozen at −157 °C, only one conformer is essentially populated in **4**, otherwise not only the methyl signal but also a number of other signals would have split (possibly with unequal intensities). This is in keeping with the computed energy difference (1.55 kcal mol^{-1}) between the racemic and *meso* conformer (Scheme 2), which entails, for the latter, a population as small as 0.1% at −157 °C. The corresponding line shape simulation yields[22] a $\Delta G^{\ddagger}$ = 5.6 ± 0.3 kcal mol^{-1} for the enantiomerization barrier interconverting the *RR* into the *SS* enantiomer (Scheme 2). By assuming that the transition state corresponds to the situation whereby one of the two C=O bonds is coplanar with the benzene ring, the calculated barrier turns out to be 4.4 kcal mol^{-1}, in reasonable agreement with the experimental value. In the less hindered derivative **3** (R = Et) the enantiomerization process is computed to have a barrier (3.1 kcal mol^{-1}) which is 1.3 kcal mol^{-1} lower than that computed in **4**, and this explains why the barrier of **3** could not be experimentally measured.

The evidence from the solution spectra does not allow one to decide on experimental ground whether the unique populated conformer of **4** has the *meso* or the racemic structure, although the computations predict that all the ketones **2**−**4** are more stable in the racemic than in the *meso* form.

A possible method for obtaining experimental support to the structure proposed by the theory is based on the NMR spectroscopy in the solid state. Molecules having

(22) Since both the carbonyl groups are involved in the exchange process with the same probability, a transmission coefficient of $^1/_2$ was employed.[12] The use of a unitary coefficient would yield a $\Delta G^{\ddagger}$ value 0.15 kcal mol^{-1} higher.

(23) Owing to the greater steric compression, Ar−CO diehdral angles of 45° were computed for the *ZZ* conformer.

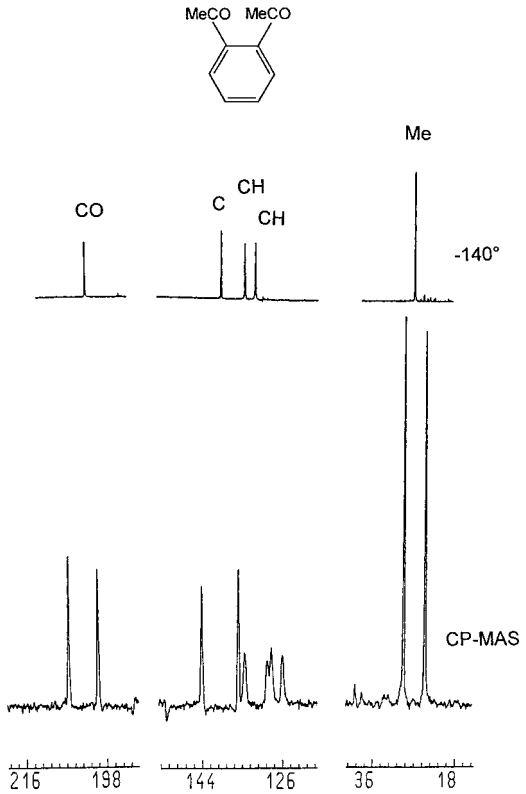


Figure 3. ^{13}C spectrum (75.5 MHz) of **2** at −140 °C in a Me_2O solution (top): underneath is displayed the solid state (CP-MAS) spectrum at room temperature, also at 75.5 MHz.

a pair of enantiotopic carbons not related by a plane (or center) of symmetry usually display, in the crystal, two different NMR peaks. If such a plane (or center) of symmetry is present the same multiplicity of the solution spectrum (i.e. a unique peak for both such carbons) is maintained in the solid state.[12,24,25] As a consequence we expect that in a ^{13}C CP-MAS spectrum the *meso* conformer would yield a single peak whereas the racemic conformer would yield two different peaks for each pair of carbons. The latter was indeed the case observed in **2** where the ten carbons yield five pairs of 1:1 doublet signals[26,27] (Figure 3). An analogous result was obtained for **3** (R = Et), whose solid state spectrum had to be obtained, however, at −70 °C since this compound does not crystallize at room temperature. The conclusions that can be derived from the spectra in the solid thus match quite well the MM predictions of a preferred racemic conformation for derivatives **2**−**4**.

Experimental Section

Material. Compounds **1** and **2** were commercially available whereas **3** and **4** were synthesized using the same procedure. As an example the synthesis of **3** is reported in detail.

1-[2-(1-Hydroxypropyl)phenyl]propan-1-ol (3′). To a solution of 40 mL (40 mmol) of 1 M EtMgBr in 10 mL of dry THF kept at −35 °C under N_2 was added dropwise a solution of 2.4 g (18.2 mmol) of phthalic aldehyde in 5 mL of dry THF. After 20 min the temperature was raised to 20 °C and the reaction quenched with a saturated solution of NH_4Cl in water. The organic layer was separated, washed with water (4 × 20 mL), and dried (Na_2SO_4), and subsequently the solvent was removed by distillation at reduced pressure. The crude product (1.8 g) was purified by chromatography on silica gel (eluent ether:petroleum ether 2:1) to yield 0.5 g of a pale yellow oil: ^1H NMR ($CDCl_3$) δ 0.97 (t, 3 H, Me), 2.80 (m, 2 H, CH_2), 2.29 (s, 1H, OH), 4.88 (dd, 1 H, CH), 7.27 (m, 1H, Ar); 7.42 (m, 1H, Ar); ^{13}C NMR ($CDCl_3$) δ10.7 (Me), 31.4 (CH_2), 72.4 (CH), 126.3 (CH,Ar), 127.7 (CH,Ar), 141.4 (quat, Ar). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.08; H, 9.28.

1-(2-Propionylphenyl)propan-1-one (3). To a mixture, kept under nitrogen, of **3′** (0.3 g, 1.5 mmol in 5 mL of dry benzene) and of $RuCl_2(PPh)_3$[28] (173 mg, 0.18 mmol) was slowly (1 h) added a solution of *t*-BuOOH (0.54 g, 6 mmol in 5 mL of dry benzene). After an additional hour of stirring, the reaction was quenched by adding black Pd powder. The solid was filtered off and the filtrate concentrated under reduced pressure. The residue was purified by chromatography on a preparative SiO_2 TLC (eluent ether:petroleum ether 2:1) to obtain a pale yellow oil (0.2 g): ^1H NMR ($CDCl_3$) δ 1.22 (t, 3 H, Me), 2.85 (q, 2 H, CH_2), 7.55(s, 2H, Ar); ^{13}C NMR ($CDCl_3$) δ 8.2 (Me), 34.4 (CH_2), 127.5 (CH,Ar), 130.8 (CH,Ar), 139.2 (quat, Ar), 204.6 (quat, CO). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.80, H, 7.50.

1-(2-Isobutyrylphenyl)-2-methylpropan-1-one (4): ^1H NMR ($CDCl_3$) δ 1.20 (d, 6 H, Me), 3.18 (m, 1 H, CH), 7.55 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$) δ 18.7 (Me), 38.3 (CH), 127.9 (CH, Ar), 130.6 (CH, Ar), 139.4 (quat, Ar), 208.1 (quat, CO). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H,8.31. Found: C, 77.09; H, 8.35.

NMR Spectra. The low-temperature solution spectra of compounds **1**−**3** were run at 300 MHz (^1H) or 75.5 MHz (^{13}C); the ^{13}C spectrum of **4** was recorded at 100.6 MHz. The samples were prepared by condensing the gaseous solvents (CHF_2Cl, Me_2O), by means of liquid nitrogen, into NMR tubes (containing the desired products with a small amount of CD_2Cl_2 for the lock operation) connected to a vacuum line. The samples were then sealed under vacuum and introduced into the precooled probe of the spectrometer. The line shape analysis was performed by means of computer programs based on the Bloch equations.[29] At temperatures lower than −162 °C compound **1** is almost insoluble in CHF_2Cl thus, in order to have an approximate value of the line width in absence of exchange for the computer simulation, the following criterion was adopted.[30] At temperatures where the Ar−CHO rotation is still rapid, so that the HCO signal is not yet exchange broadened (i.e., −120, −130 °C), the ratio between its line width and that of CHF_2Cl was determined (about 1.5). On the assumption that this ratio remains essentially constant on further lowering the temperature, the line width of CHF_2Cl, measured at −162 °C (43 Hz), was multiplied by such a factor, therefore assigning a 65 Hz intrinsic line width to the HCO signals of **1** at that temperature. We also checked that uncertainties as large as 50% on this line width only affect the resulting $\Delta G^{\ddagger}$ value by 0.1 kcal mol^{-1}. The ^{13}C-NMR solid

(24) Casarini, D.; Lunazzi, L.; Macciantelli, D. *J. Org. Chem.* **1988**, *53*, 177.

(25) We stress that such a statement is not wholly unambiguous since it is possible to find, occasionally, molecules with a plane of symmetry that have their NMR lines split in the solid state in that the molecular symmetry might not be coincident with the site symmetry (for further details see ref 24 and references cited therein).

(26) On the contrary the solid state spectrum of the isomeric 1,4-diacetylbenzene displayed a single line for the CH_3 carbons, as expected for a structure retaining, in the crystal, a molecular plane of symmetry (Lipmaa, E. T.; Alla, M. A.; Pehk, K. T.; Engelhardt, G. *J. Am. Chem. Soc.* **1978**, *100*, 1929. See also: Penner, G. H.; Wasylishen, R. E. *Can. J. Chem.* **1989**, *67*, 525).

(27) The cause underlying the splitting of the CO signal observed in the solid state spectrum of **1** is different from that of **2** and **3**. In **1** it is a consequence of the *syn*−*anti* relationship of the HCO groups in the **1**-ZE conformation and corresponds to the same situation detected in solution (see Figure 1). In **2**, on the other hand, it is due to the properties of an asymmetric molecule in the crystal and cannot be detected in the solution spectra. Such a difference is clearly reflected in the amount of the splitting which is quite small (1.8 ppm) in **1** but, for instance, much larger (6.5 ppm) in **2**. Likewise the separation of the ring carbon signals is so small as to be almost undetectable in **1** but, again, large in **2** (3.4−8.3 ppm).

(28) Murahashi, S.-I.; Naota, T. *Synthesis* **1993**, 433.

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(30) Lunazzi, L.; Macciantelli, D.; Bernardi, F.; Ingold, K. U. *J. Am. Chem. Soc.* **1977**, *99*, 4573.

state CP-MAS spectra of **1** and **2** were obtained at 75.5 MHz. The solid samples were finely ground and packed into a 7 mm zirconia rotor that was spun at the magic angle with a spinning rate of about 3−4 KHz. The ^{1}H pulse duration for a 90° flip angle was 4 μs which was also the value for ^{13}C as set by Hartmannn−Hahn conditions.[31] For the cross polarization a contact time of 2 ms was employed, while the recycle delay for CP experiments was typically 5 s. The number of transients was varied in order to achieve good signal-to-noise ratios. Spinning side bands were eliminated by using a basic TOSS sequence.[32] Dipolar dephasing experiments[33] were used to confirm peak assignment to quaternary carbons and mobile methyl groups. Chemical shifts were measured with respect to the lower frequency signal for adamantane at 29.4 ppm, with respect to TMS (by replacement). The low-temperature (−70 °C) required to record the spectrum of **3** was obtained by means of a flow of dry nitrogen precooled in a heat exchanger immersed in liquid nitrogen.

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(33) (a) Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854. (b) Alemany, L. B.; Grant, D. M.; Alger, T. D.; Pugmire, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 6697.