^{13}C NMR and AM1 Study of the Intramolecular Proton Transfer in Solid 1,3-Diphenylpropane-1,3-dione

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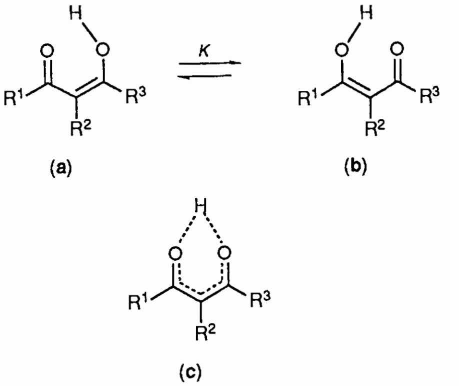
The intramolecular proton transfer reaction which takes place in solid 1,3-diphenylpropane-1,3-dione has been studied using a combination of ^{13}C CPMAS NMR spectroscopy and AM1 calculations. The splittings observed in the carbon signals, which are equivalent in solution, are interpreted in terms of a double minimum potential model, with the solution degeneracy of tautomers being lifted in the crystals. MO calculations suggest that the displacement of the equilibrium towards one of the tautomeric structures is due to conformational distortion upon crystallization.

Proton transfer reactions are relevant to such phenomena as phase transitions in ferroelectrics,[1,2] dye phototautomerism at cryogenic temperatures,[3–6] pumping of protons across biomembranes,[7,8] the mechanism of vision,[9] and a great variety of chemical and biochemical catalytic systems.[10–12] Interest has grown in recent years in hydrogen exchange processes in crystalline organic materials, as studied by high-resolution solid-state NMR spectroscopic techniques.[13] As a complement to the traditional approach to hydrogen motion in solid samples involving X-ray or neutron diffraction techniques, NMR methods offer the advantage of probing dynamic as well as structural details.

Much attention has been focussed on the shape of the potential energy function for the proton migration.[14] In systems containing O–H···O hydrogen bonds in which one of the oxygens carries a formal charge—as in acid salts of dicarboxylic acids—diffraction data implied nearly linear O–H–O arrangements and very short O···O distances.[15] It has been suggested that in these cases, where O···O distances are <*ca.* 2.45 Å, the proton is confined to a single minimum potential. This has been confirmed by the observation of negative ^{1}H, ^{2}H and ^{1}H, ^{3}H isotope effects in solution for hydrogenmaleate and hydrogenphthalate anions.[16] Recent solution NMR observations in a protonated form of 2-methyl-1,3-diphenylpropane-1,3-dione also lend support to the idea of a strong (most probably linear) hydrogen bond in charged structures.[17] In neutral systems bearing the 1,3-diketo fragment in its enol form, where a strong intramolecular hydrogen bond occurs, experimental results in the solid phase have been interpreted on the basis of both single[18] (**c**) and double[19,20] [(**a**) = (**b**)] proton sites. Where accurate neutron diffraction data are available, the second model seems to be preferred[20] for neutral molecules, a view which is supported by solid-state NMR investigations,[21,22] and the measurement of positive solution ^{2}H and ^{3}H isotope effects.[16,23]

If reliable hydrogen positions cannot be obtained through diffraction data, a proper structural characterization may not be possible, since bond distances between heavy atoms will show averaged values. On the other hand, NMR spectroscopic methods are sensitive to dynamic phenomena, and have been used to obtain kinetic information on solid proton transfers, mainly by applying variable temperature line-shape analysis.[24–28] However, if the exchange is fast on the NMR time scale, average lines will be measured, and this will only allow for the setting of a minimum limit to the exchange rate.



In the stable form of 1,3-diphenylpropane-1,3-dione (**1**; $R^1 = R^3 = Ph$; $R^2 = H$), diffraction results revealed an average structure.[29–31] Neutron diffraction showed unequal C–O bond lengths [δr(C–O) = 0.039 Å] and dihedral phenyl–enol ring angles (Figure 1), and an asymmetric location of the labile hydrogen, which presents a large anisotropic thermal ellipsoid.[31] On the other hand, a doubling in the signals arising from C-1 and C-3 has been reported in the ^{13}C solid state NMR spectrum of (**1**). This compound crystallizes in space group *Pbca* with $Z = 8$, and the asymmetric unit is composed of a single molecule with no particular symmetry imposed. Therefore, the doubling does not arise from the presence of non-congruent molecules in the unit cell, and was attributed to the asymmetric nature of the hydrogen bonding within a fixed structure of type (**1c**).[32] A new, metastable polymorph of (**1**) has been recently described,[33] showing δr(C–O) = 0.005 Å. In the present paper, the original ^{13}C chemical shift assignment in solid (**1**) is reviewed, and a previously unnoticed splitting in the resonances of C-4 and C-10 is reported. The adoption of the double potential model leads to independent predictions of the equilibrium constant in the solid state from the observed splittings in the two pairs C-1, C-3 and C-4, C-10. This result is discussed in light of the available crystal structure, together with information provided by the AM1 semi-

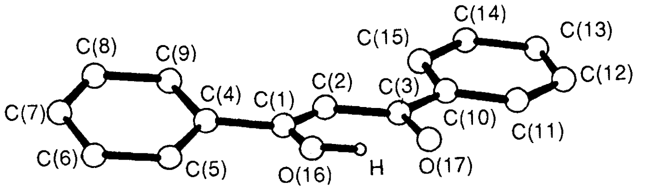


Figure 1. Drawing of the molecular structure of (1) as obtained by neutron diffraction measurements. The labile hydrogen is shown as bonded to the oxygen which corresponds to the preferred tautomer observed by diffraction methods, and also predicted by the present AM1 calculations. Defining ring A: C-1, C-2, C-3, O-16, O-17, H; ring B: C-4, C-5, C-6, C-7, C-8, C-9; ring C: C-10, C-11, C-12, C-13, C-14, C-15; the dihedral angles subtended are: A–B, 17.0°; A–C, 3.9°.

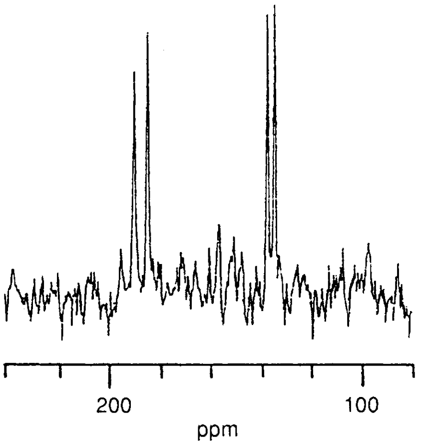


Figure 2. High-resolution ^{13}C CPMAS spectrum of 1,3-diphenylpropane-1,3-dione (1) at 75.5 MHz using the interrupted ^{1}H decoupling mode which only shows quaternary carbons (and, if present, methyl groups). Splittings of 5.4 and 2.8 ppm are clearly resolved in the signals arising from the pairs of C-1, C-3, and C-4, C-10 respectively.

empirical MO program.[34] It is shown that the observed differential twisting of the two phenyl groups with respect to the enol ring leads to a preferred tautomer having the labile proton bonded to the oxygen which corresponds to the longer C–O length. Therefore, the lifting of the degeneracy of the isolated tautomers (**1a**) and (**1b**) is explained as the result of the molecular conformation present in the solid, and this helps the understanding of the observed crystal structure. In addition, calculated charge densities at C-1, C-3, C-4, and C-10 could be of help in the analysis of the observed splittings.

Experimental

Compound (1), 1,3-diphenylpropane-1,3-dione (Aldrich) was crystallized from ethanol for the NMR measurements. The solid-state ^{13}C spectrum shown in Figure 2 was recorded on a GN300WB spectrometer operating at 75.5 MHz in the CPMAS mode. The sample was packed in a Kel-F rotor and spun at *ca.* 3 kHz. The TOSS sequence was applied to avoid spinning sidebands.[35] Spectral parameters were: SW, 30 kHz; number of acquisitions, 13 300; acquisition time, 67.58 ms; proton 90° pulse, 10 μs (bilevel decoupling allowed to increase the ^{1}H decoupling field during acquisition); cross-polarization time, 3 ms; recycle delay, 2 s; 4K memory. High power ^{1}H decoupling was interrupted during one of the delays of the TOSS train, *ca.* 50–60 μs, in order to suppress non-quaternary carbon signals.[36] Chemical shifts were measured downfield from Me_4Si, using hexamethylbenzene as a secondary standard (Me signal at 17.4 ppm).

AM1 calculations were performed utilizing the AMPAC package, version 2.10, with gradient optimization on an IBM 3031 computer. In all cases the PRECISE option was used to provide higher data accuracy within the AM1 model. Further optimization restrictions are discussed below.

Results and Discussion

Compound (1) has been previously studied by ^{1}H,[37] and ^{13}C,[32,38,39] NMR spectroscopy in solution, where average resonances have been detected due to the fast equilibrium (**1a**) $\rightleftharpoons$ (**1b**). The chemical shifts assigned to C-1 and C-3 are 185.2 in $(CD_3)_2SO$[32] 185.3 in $CDCl_3$,[38] and 186.0 ppm in C_6D_6[39] whereas for the pair C-4 and C-10 the corresponding values are 134.7[32] and 135.4 ppm.[38] In the solid state, the ^{13}C NMR spectrum shows two clearly resolved lines for the C-1 and C-3 atoms of C–O at 182.9 and 188.2 ppm,[32] a splitting which was attributed to the existence of an inherently asymmetric hydrogen bond in the (**1c**) structure. Signals from C-4 and C-10 were not unambiguously assigned because of the overlapping with those arising from the C–H aromatic carbons. However, since diffraction results show that the molecular conformation is devoid of the ideal solution symmetry, mainly due to a distinct twisting of the phenyl rings with respect to the enol ring, it was interesting to investigate whether there was a corresponding effect on C-4 and C-10. As shown in Figure 2, the use of the interrupted decoupling sequence devised by Opella[36] allows the clear identification of two signals arising from C-4 and C-10, at 133.2 and 136.0 ppm. In what follows, the double-minimum potential model will be adopted. Previous experimental results derived from ^{2}H nuclear quadrupole resonance studies of deuteriated (1) in the solid state have supported the latter model.[19] Furthermore, ^{2}H and ^{3}H isotope effects [$\delta(^{1}H) - \delta(^{2,3}H)$] were found to be positive for (1) in solution,[16] a result which is also in accordance with the existence of a double minimum potential for the hydrogen motion. If the labile hydrogen were constrained to a single potential well, ^{2}H and ^{3}H, with smaller vibrational amplitudes as compared with ^{1}H, would 'concentrate' near the position of the minimum, and this would cause a relative deshielding. Conversely, for double minimum energy profiles, the heavier isotopes tend to adopt equilibrium positions which are nearer to each of the oxygen atoms, leading to a relative shielding with respect to ^{1}H.[16] In order to appreciate the consequences of this result within this two-site model, we let *i,j* denote a pair of carbons which are equivalent in solution owing to symmetry considerations. The average chemical shift δ_i in the solid is given by equation (1).

$$\delta_i = (\delta_{ia} + K\delta_{ib})/(1 + K) \qquad (1)$$

A similar equation holds for δ_j, where δ_{ia} and δ_{ib} are the chemical shifts of carbon *i* in (**1a**) and (**1b**), respectively. The splitting $\delta_{ij} = (\delta_i - \delta_j)$ is therefore given by equation (2).

$$\delta_{ij} = [(\delta_{ia} - \delta_{ja}) + K(\delta_{ib} - \delta_{jb})]/(1 + K). \qquad (2)$$

In solution, $(\delta_{ia} - \delta_{ja}) = (\delta_{jb} - \delta_{ib}) = \delta_0$ and then $\delta_{ij} = \delta_0(1 - K)/(K + 1)$, from which equation (3) is derived.

$$K = (\delta_0 - \delta_{ij})/(\delta_0 + \delta_{ij}) \qquad (3)$$

Equation (3) has been previously used to estimate K in other proton exchanging systems.[24–28] The value of δ_0 can be computed if the exchange reaction is frozen at low temperatures,[24,25] or by considering non-exchanging model compounds both in solution and in the solid phase.[39,40] The use of the latter approach gives approximate values of $\delta_0 = 24$

Table 1. Relevant results obtained after performing AM1 calculations on compound **(1)**.[a]

Parameter	Tautomer (**a**)	Tautomer (**b**)
Heat of formation/kcal mol^{-1} [b]	−8.04	−7.04
C(1)–O(16) bond length/Å	1.365	1.256
C(3)–O(17) bond length/Å	1.250	1.364
C(1)–C(2) bond length/Å	1.362	1.453
C(2)–C(3) bond length/Å	1.454	1.362
O(16)–O(17) distance/Å	2.769	2.741
O(16)–(H) distance/Å	0.974	1.956
O(17)–(H) distance/Å	1.978	0.974

[a] Geometry optimization was performed fixing the dihedral angles between the phenyls and the enol ring at the experimental values. [b] Cal = 4.184 J.

ppm for i,j = 1,3 [39] whereas for i,j = 4,10 it can be estimated that δ_0 = 6.4 ppm, twice the difference between the values observed in chalcone[41] and in compound **(1)** itself. Therefore, the following values of K can be calculated: 0.65 (i,j = 1,3) and 0.33 (i,j = 4,10). The discrepancy can be ascribed to the incorrect assumption that $(\delta_{ia} - \delta_{ja}) = (\delta_{jb} - \delta_{ib}) = \delta_0$, due to the fact that the molecular conformation in the solid state is not symmetric (Figure 1). If δ_a and δ_b are the differences between the solution value δ_0 and the shifts occurring in asymmetric, fixed conformations of either **(1a)** or **(1b)** in the solid state then equations (4) and (5) follow.

$$(\delta_{ia} - \delta_{ja}) = \delta_0 - \delta_a \qquad (4)$$

$$(\delta_{jb} - \delta_{ib}) = \delta_0 - \delta_b \qquad (5)$$

The observed splitting in the solid will therefore be given by equation (6).

$$\delta_{ij} = \delta_0(1 - K)/(K + 1) + (K\delta_b - \delta_a)/(K + 1) \qquad (6)$$

This shows that a partition $0.5(\delta_b - \delta_a)$ will be observed, even if the value of K is accidentally 1. It follows that the experimental splittings in the pairs 1,3 and 4,10 may have contributions both from crystallographic effects ($\delta_a \neq \delta_b$) and changes in equilibrium composition ($K \neq 1$) in going from solution to the solid state, making it difficult to discern between them. In order to gain further information on the shift in equilibrium in crystalline **(1)** and on the origin of the measured splittings, theoretical calculations were performed.

Semiempirical methods have proved to be non-expensive and accurate enough to carry on calculations upon relatively large molecules. AM1 (Austin Model 1),[34] developed by Dewar's group, seems to be the method of choice for the present work since it has been successfully used in hydrogen-bonded systems,[42–45] overcoming the already known failures of the previous semiempirical procedures (MNDO and MINDO/3) to give a proper account of hydrogen bonding.[46–48]

In order to better approximate the asymmetric environment of the hydrogen bond in solid **(1)**, the differential twisting of the phenyl rings should be included in the calculations. Therefore, when the molecular geometries were optimized, the dihedral angles subtended between the phenyl rings and the keto–enolic moiety were constrained to those values observed in the neutron diffraction study (see Figure 1).[31] This restriction, *i.e.*, the breakage of the effective C_{2v} symmetry, was imposed to the trial geometries in which the labile hydrogen was bonded either to O(16) or to O(17). These calculations yielded different heats of formation for the extreme structures **(1a)** and **(1b)** (see Table 1). Since there are no significant intermolecular interactions in crystalline **(1)**,[31] it is reasonable to assume that the disruption of the degeneracy of the tautomers can be adequately modelled by the molecular dissymmetry induced by the crystal packing. To this effect we also ascribe the splittings in the ^{13}C signals described by equation (6).

As shown in Table 1, which summarizes the most relevant AM1 results, the minima corresponding to the structures having the labile hydrogen bonded to O(16) or O(17) show optimized geometries possessing C–C and C–O bond lengths which are typical of those observed in ordered systems [δr(C–O) > 0.1 Å].[20] From these data it can be inferred that the behaviour of this molecule is better described by means of an asymmetric double-minimum potential energy profile, in agreement with our previous assumption.

The distinct stabilities of **(1a)** and **(1b)** predicted by AM1 agree with the NMR results, *i.e.*, $K \neq 1$ in the solid, and also with the neutron diffraction study, which shows different averaged C–O bond lengths. Moreover, the favoured tautomeric structure is the one in which the labile hydrogen is bonded to O(16) (Table 1), which exhibits the larger C–O distance. Therefore, this oxygen is more prone to behave as an enolic rather than as a carbonylic one. It might be assumed that the observed C–C and C–O bond lengths of the keto–enolic moiety are the averaged values of those calculated for the extreme structures **(1a)** and **(1b)**. From data in Table 1, this approximation allows one to estimate equilibrium constants falling between 0.25 and 0.43, which are in the same range as those predicted above from the NMR data.

As for the expected splittings in the carbon shifts of the pairs C-1, C-3 and C-4, C-10, the calculated electron densities on these carbons may shed some light on the subject. The frozen conformation achieved in the crystal induces a non-equivalent chemical environment for the nominally equivalent quaternary carbons as seen in solution. In such a way, if $(\delta_{ia} - \delta_{ja}) \neq (\delta_{jb} - \delta_{ib})$, as suggested above, the same relationship must hold for the electron densities at these carbons. In fact, as shown in Table 2, the calculated values differ by *ca.* 10% between the pairs C-1, C-3 and C-4, C-10, and this confirms that the observed partitions δ_{ij} will have contributions both from crystallographic effects and solution/solid equilibrium shift. Also, the last two columns in Table 2 show that a reasonable correlation may be expected to hold between the averaged net charges at these carbons and the observed chemical shifts.

The present results may be relevant to the question of the coupling between proton motion and skeletal deformations, a possibility which has been previously suggested both on theoretical[49] and experimental[24,25] grounds. We have shown that the non-degeneracy of tautomers in **(1)** is modelled by the unique molecular conformation attained in crystals, and that AM1 calculations are able to predict the correct preferred tautomer. Further work is being pursued on related molecules in order to establish similar trends.

Conclusion

The intramolecular single proton transfer occurring in solid 1,3-diphenylpropane-1,3-dione has been examined by use of high-resolution ^{13}C CPMAS spectroscopy and semiempirical AM1 calculations. The results strongly suggest that the observed average diffraction structure and ^{13}C resonances should be interpreted in terms of a fast-exchange reaction between both possible tautomers. The degeneracy of these tautomers is removed by the crystal packing, leading to a differential twisting between both phenyl rings with respect to the enol ring. Calculations allowing the labile proton to reside at both chemical sites give optimized geometries for the enol ring showing differences in C–O bond lengths which are

Table 2. Calculated net atomic charges by means of AM1 upon the quaternary carbons in (**1**).[a]

Carbon	q_a	$q_{ia} - q_{ja}$	q_b	$q_{jb} - q_{ib}$	q_{av}[b]	δ(ppm)[c]
C-1	0.207	−0.116	0.316	−0.102	0.243	182.9
C-3	0.323		0.214		0.287	188.3
C-4	−0.077	0.060	−0.131	0.055	−0.095	136.0
C-10	−0.137		−0.076		−0.117	133.2

[a] *i,j* denote a pair of carbons which are equivalent in solution (*i,j* = 1,3 or 4,10); subscripts **a** and **b** refer to tautomers (**1a**) and (**1b**) respectively. [b] $q_{av} = (q_a + Kq_b)/(1 + K)$, assuming $K = 0.5$. [c] Increasing values of δ were assigned to more positively charged carbons.

consistent with observations in ordered systems (*ca.* 0.1 Å). Moreover, one of these tautomers is shown to be preferred in the solid state: it is the one bearing the labile hydrogen as bonded to the oxygen which corresponds to the (observed) longest C–O distance. The connection between calculated charge densities at the quaternary carbons in the tautomers and the splittings observed in the NMR spectrum is also discussed.

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