A 13C NMR Study of the "Arene–Olefin" Valence Tautomerism of 1,6-Methano[10]annulenes in the Solid Phase

Lucio Frydman,[†] Benjamin Frydman,*,[†] Irina Kustanovich,[‡] Shimon Vega,[‡] Emanuel Vogel,[§] and Constantino Yannoni[‖]

Contribution from the Facultad de Farmacia y Bioquimica, Universidad de Buenos Aires, Junin 956, 1113 Buenos Aires, Argentina, the Department of Isotope Research, The Weizmann Institute of Sciences, 76100 Rehovot, Israel, the Institut für Organische Chemie, Universität Köln, Greinstrasse 4, D-5000, Köln 41, FRG, and the IBM Almaden Research Center, San Jose, California 95120. Received December 6, 1989

Abstract: High-resolution 13C NMR techniques were used in order to investigate the "arene–olefin" valence tautomerism between 11,11-disubstituted 1,6-methano[10]annulenes and their respective bisnorcaradienes in the solid phase. It was found that the bridgehead carbon resonances of the dimethyl and of the methylcyano derivatives shift with temperature in a manner that suggests the occurrence of an exchange process proceeding fast on the NMR time scale. In all the cases, the crystal packing forces were found to affect considerably the thermodynamic parameters of the kinetic processes. Although it was not possible to reach a low enough temperature so as to observe the resolved resonances of the aromatic and of the olefinic tautomers, the present solid-state NMR results were combined with previous solution NMR studies in order to obtain the free energies involved in the tautomeric processes. Moreover, a good correlation could be established between the solid-state NMR and the X-ray diffraction results of the compounds. Finally, some of the implications that the present work might have for the understanding of valence tautomerism in 1,6-methano[10]annulenes are briefly discussed.

Introduction

Since the first 1,6-methano[10]annulenes were synthesized 25 years ago,[1] several experimental[2-12] and theoretical[13-17] studies have been devoted to the clarification of the detailed molecular structure of this class of compounds. 1,6-Methano[10]annulenes (I, Figure 1) possess a system of 10 π electrons and a methano bridge that, by joining carbons C1 and C6, avoids the strain that would be introduced by the presence of two inner hydrogens. Despite the aromaticity that these compounds exhibit, the deviations from the normal sp² angles that are introduced by the methano bridge give rise to the rapid equilibrium shown in Figure 1, according to which the aromatic forms can coexist with their corresponding olefinic bisnorcaradienes II. This valence tautomerism has been explored in solution by means of NMR and UV spectroscopy[3-7] as well as in the solid phase by means of X-ray diffraction analyses.[2,8-12] In the solution studies, 13C NMR appeared to be very useful in characterizing the equilibrium of the tautomerism, since the resonance frequencies of the bridgehead C1/C6 carbons are expected to range from 120 ppm in tautomer I to 20 ppm in II.[7] In the solid-state investigations, the variations in the C1–C6 distance appeared as the most sensitive parameter for probing the I ⇌ II equilibrium, as this distance was observed to range from 2.27 Å in the aromatic structure to 1.54 Å in the bisnorcaradiene form.[18] As a consequence of this body of investigations, a remarkable property about the valence tautomerism in [10]annulenes emerged: namely, that the equilibrium constant of the reaction is highly dependent on the electronic nature of the R and R' substituents at C11. This fact has been explained in terms of the stabilizying effects of electron-withdrawing groups on the formation of the cyclopropane ring of II[19] and has been used as a tool in order to control the equilibrium position of the tautomerism.

Of the various 1,6-methanol[10]annulenes that have been examined, the 11,11-dimethyl and the 11-methyl-11-cyano derivatives (DIM and MC) afforded some of the most interesting results. For these compounds, both the C1/C6 solution 13C chemical shifts[6] and the C1–C6 distances in the crystals[8,10,11] were found to fall in between the extreme values that can be expected for either the aromatic or the olefinic tautomers. In addition, it was noted that both the spectroscopic and the structural parameters used for the

characterization of the valence tautomerism of these compounds showed a temperature dependence.[7,11] Different explanations were advanced to interpret these results, each one reflecting, in a way, the origin of the study. Whereas the solution results were explained on the basis of an I ⇌ II equilibrium proceeding fast on the NMR time scale,[6] the X-ray results were assumed to represent snapshots of the I ⇌ II equilibrium at different stages of advancement.[13,20] High-resolution solid-state 13C NMR appears as a useful method in order to bridge this gap between the solution and the X-ray interpretations. Indeed, this technique has already been successfully applied to the evaluation of a number of tautomeric processes in the solid state.[21-23]

(1) Vogel, E.; Roth, H. D. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 228.

(2) Dobler, M.; Dunitz, J. D. *Helv. Chim. Acta* **1965**, *48*, 1494.

(3) Günther, H. *Z. Naturforsch.* **1965**, *20b*, 948.

(4) Blatman, H. R.; Böll, J. C.; Heilbronner, E.; Hohlneicher, G.; Vogel, E.; Weber, J. P. *Helv. Chim. Acta* **1966**, *49*, 2017.

(5) Vogel, E. *Pure Appl. Chem.* **1969**, *20*, 237.

(6) Günther, H.; Schmickler, H.; Bremser, W.; Straube, F. A.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 570.

(7) Günther, H.; Schmickler, H. *Pure Appl. Chem.* **1975**, *44*, 807.

(8) Bianchi, R.; Morosi, G.; Mugnoli, A.; Simonetta, M. *Acta Crystallogr., Sect B* **1973**, *B29*, 1196.

(9) Pilati, T.; Simonetta, M. *Acta Crystallogr., Sect B* **1976**, *B32*, 1912.

(10) Bianchi, R.; Pilati, T.; Simonetta, M. *Acta Crystallogr., Sect B* **1978**, *B34*, 2157.

(11) Bianchi, R.; Pilato, T.; Simonetta, M. *J. Am. Chem. Soc.* **1981**, *103*, 6426.

(12) Vogel, E.; Scholl, T.; Lex, J.; Hohlneicher, G. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 869.

(13) Burghi, H. B.; Shefter, E.; Dunitz, J. D. *Tetrahedron* **1975**, *31*, 3089.

(14) Gavezzotti, A.; Simonetta, M. *Helv. Chim. Acta* **1976**, *59*, 2984.

(15) Gatti, C.; Barzaghi, M.; Simonetta, M. *J. Am. Chem. Soc.* **1985**, *107*, 878.

(16) Simonetta, M.; Gatti, C.; Barzaghi, M. *J. Mol. Struct.* **1986**, *138*, 39.

(17) Haddon, R. C.; Scott, L. T. *Pure Appl. Chem.* **1986**, *58*, 137.

(18) Simonetta, M. *Pure Appl. Chem.* **1980**, *52*, 1597.

(19) Hoffman, R.; Davidson, R. B. *J. Am. Chem. Soc.* **1971**, *93*, 5699.

(20) Burghi, H. B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153.

(21) Macho, V.; Miller, R. D.; Yanoni, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3735.

(22) Meier, B. H.; Earl, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 5553.

(23) Frydman, L.; Olivieri, A. C.; Diaz, L. E.; Valasinas, A.; Frydman, B. *J. Am. Chem. Soc.* **1988**, *110*, 5651.

†University of Buenos Aires.
‡The Weizmann Institute of Sciences.
§University of Cologne.
‖IBM Almaden Research Center.

^{13}C NMR Study of "Arene-Olefin" Valence Tautomerism

J. Am. Chem. Soc., Vol. 112, No. 18, 1990 6473
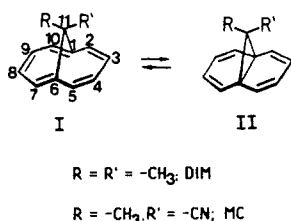
Figure 1. Valence tautomerism between 1,6-methano[10]annulenes and their corresponding bisnocaradienes showing the atoms numbering and the substituents used in the present study.

In the present work, the results of a variable-temperature ^{13}C CPMAS NMR analysis on DIM and MC are reported. It was found that the C1/C6 ^{13}C resonances of these compounds shift with temperature, but with a thermodynamic behavior that is completely different from the one observed for the molecules in solution. Although these spectral changes strongly suggest the presence of a fluxional I ⇌ II process, it was not possible to reach a temperature low enough so as to observe the individual signals of the aromatic and the olefinic tautomers. Nevertheless, it was possible to obtain an estimation of the difference in energies involved in the I ⇌ II process as well as a good correlation between the solid-state NMR and the X-ray diffraction results.

Experimental Section

DIM and MC samples were synthesized from tetralin with use of the sequence of reactions described in the literature,[24] followed by recrystallization from an n-pentane solution. The MC obtained in this way shows the same CPMAS NMR spectrum as the one that can be observed from a sample obtained by slow evaporation of a room temperature methanolic solution of MC (the α form).[10] The other polymorph of MC (β-MC)[11] could be obtained either by slow evaporation of a methanol solution at 0 °C or by heating α-MC above 75 °C. The ^{13}C CPMAS NMR spectra were recorded at 50.3 MHz on a Bruker MSL-200 NMR spectrometer equipped with a Bruker variable-temperature probe and on a home-built spectrometer build around a 4.7 T magnet and equipped with a Doty variable-temperature probe. Spinning rates varied between 2.7 and 3.7 kHz (depending on the temperature), and an average of 5000 scans were acquired for obtaining each spectrum.

Results

Figure 2 shows a set of ^{13}C CPMAS NMR spectra of DIM recorded at different temperatures. From the X-ray analysis of this compound it is known that DIM crystallizes in space group P1, with two molecules (A and B) per asymmetric unit cell.[8] Each molecule presents a different geometry and, in particular, a different C1–C6 distance (1.827 Å in molecule A, 1.771 Å in molecule B). In fact, whereas the room temperature solution ^{13}C NMR spectrum of DIM presents a single C1/C6 resonance at 81.7 ppm, the ^{13}C CPMAS NMR spectrum presents two C1/C6 resonances at 79.9 and 74.5 ppm. These signals can be assigned to molecules A and B, respectively, on the basis of their aromatic and olefinic character. The chemical shifts of the other carbon resonances in the CPMAS NMR spectrum are similar to those observed in the solution spectrum. Noteworthy, the aromatic resonances exhibit a line-broadening that increases considerably between room temperature and the melting point of the compound (88 °C). These broadenings are probably due to the occurrence of molecular motions in the solid that interfere with the ^1H decoupling process,[25] and can be estimated at ca. 2 × 10^5 Hz (the order of the decoupling field). Since the crystal structure of DIM does not show any evidence of molecular disorder, it is very likely that this motion consists of 180° flips of the molecules as a whole around their main axes, a fact that would explain the C_{2v} symmetry that the molecules possess in the solid.

The most significant changes in the variable-temperature ^{13}C CPMAS NMR spectra of DIM occur in the chemical shifts of the C1/C6 resonances. In solution, these carbons give a single
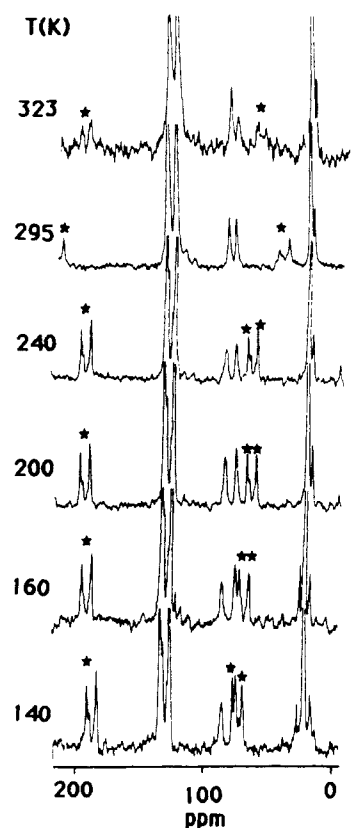
Figure 2. 50.3-MHz ^{13}C CPMAS NMR spectra of DIM recorded at different temperatures. Spectra were recorded with a 3-ms contact time and a 3-s pulse delay. All spectra were externally referenced to adamantane assuming δ_{TMS} = 0 ppm. The peaks marked with an asterisk are spinning side bands.

Figure 3. 50.3-MHz ^{13}C CPMAS NMR spectra of α-MC recorded at different temperatures. Other spectral parameters are as in Figure 2.

resonance that experiences a downfield shift as temperature is lowered, indicating that the aromatic tautomer I is the most stable one. In the solid phase, the behavior of the resonances is different.

(24) Wrubel, H. Diplomarbeit, University of Cologne, 1989, and references cited therein.
(25) (a) Rothwell, W. P.; Waugh, J. S. J. Chem. Phys. 1981, 74, 2721. (b) Frydman. L.; Frydman, B. J. Chem. Phys. 1990, 92, 1620.

Table I. ¹³C Solution and Solid-State NMR Chemical Shifts of the C1/C6 Resonance of DIM at Different Temperatures[a]

| temp, K | solution[b] | solid state | |
		molecule A	molecule B
380	79.8		
323		79.8	74.6
308	81.7		
295		79.9	74.5
240		80.0	72.8
200		80.3	71.9
163	89.3		
160		80.6	70.6
140		80.6	69.5

[a] In ppm downfield from TMS. [b] Taken from ref 6.

Table II. ¹³C Solution and Solid-State NMR Chemical Shifts of the C1/C6 Resonances of MC at Different Temperatures[a]

| temp, K | solution[b] | α-MC | | β-MC |
		molecule A	molecule B	
358				67.0
308	67.1			
298		78.8	72.5	
295				65.3
235				61.9
233	64.6			
223		81.0	72.0	
205				59.9
200		82.0	71.5	
193	62.6			
191		82.5	71.3	
185		83.3	71.0	58.6
173		84.1	70.0	
165				57.2
150		85.3	69.5	56.4
120				54.3
100				53.2

[a] In ppm downfield from TMS. [b] Taken from ref 6.

Whereas the resonance frequency of the C1/C6 signal of molecule A is almost independent of temperature (it shifts less than 1 ppm between 340 and 140 K), the C1/C6 signal of molecule B shifts upfield as the temperature is decreased. These changes, together with the temperature dependence of the chemical shifts observed in solution, are summarized in Table I.

Two polymorphs (α and β) have been reported for the MC derivative. Figure 3 shows a set of ¹³C CPMAS NMR spectra of the α form of MC recorded at different temperatures. As happened to be the case in DIM, this polymorph crystallizes in space group *P*1 with two molecules per asymmetric unit cell, each one characterized by its own C1–C6 distance (1.851 Å in molecule A, 1.783 Å in molecule B).[10] This difference is clearly visible in the room temperature ¹³C CPMAS NMR spectrum of α-MC, which shows a C1/C6 resonance at 78.8 ppm (molecule A) and another at 72.5 ppm (molecule B). There are other spectral features that are different from those observed in the solution NMR spectrum. In the solid, the effects of the residual dipolar coupling between the ¹³C and the ¹⁴N broaden the cyano resonance and make it almost disappear in the background noise.[26] In addition, there are some small extra peaks in the 10–15-ppm region that are absent in the solution spectrum. Nevertheless, the most remarkable differences between the solution and the solid-state NMR spectra appear again in the region of the C1/C6 resonances. In solution, C1 and C6 give a single peak that shifts upfield as the temperature is increased, indicating that the most stable tautomer of MC is of a bisnorcaradienic character.[6] In the solid state, each molecule of α-MC exhibits its individual behavior. Whereas the resonance of molecule B is only slightly dependent on temperature, the C1/C6 signal of molecule A shifts downfield
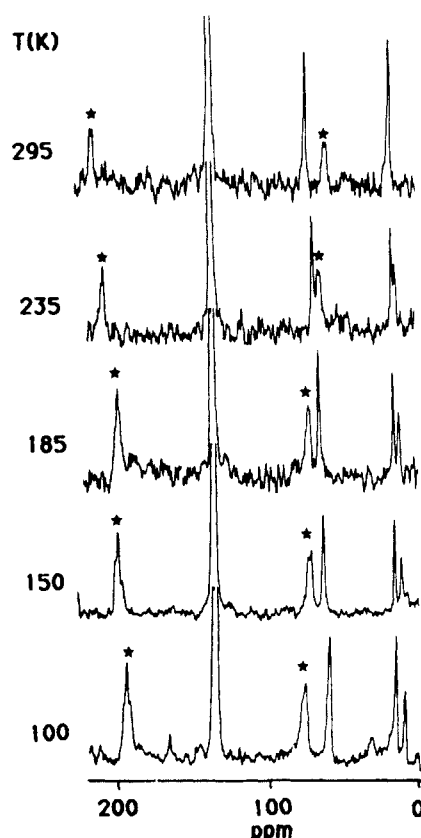
Figure 4. 50.3-MHz ¹³C CPMAS NMR spectra of β-MC recorded at different temperatures. Other spectral parameters are as in Figure 2.

as the temperature is lowered, implying that the aromatic structure of this molecule has become the most stable tautomer. A summary of the changes in the chemical shifts of the C1/C6 resonances of α-MC is given in Table II.

As the temperature of α-MC is lowered below 190 K the C1/C6 resonances of A and B become smaller (and probably broader) in a manner that is reminiscent of the changes that can be observed when a reaction moves from the fast into the intermediate NMR exchange regime. The signals are almost completely lost at ca. 180 K, but then, instead of observing a subsequent splitting of the resonances into the two signals that can be expected for slow-exchanging I and II tautomers, the peaks start to reemerge very close to their previous resonance frequencies. This process is completely reversible and was found to be independent of the times that characterize the CP experiment (T_1, $T_{1\rho}$, T_{CH}). In principle, there are two explanations for these spectral changes. The first possibility is that the signals are lost due to an NMR-related effect whose time scale is higher than the difference between the isotropic chemical shifts of I and II. Such an effect could be the interference between the exchange process I ⇌ II and the MAS averaging process,[27] since the NMR time scale of this effect is of the order of the width of the chemical shielding tensors of the sites. Indeed, an example of such a case has recently been reported.[28] A second possibility that could explain the observed broadenings is the presence of a crystal-related change, like for example a second-order phase transition. This possibility would explain the fact that both molecules are equally affected at the same temperature and could be related to the observation that α-MC might be unstable at low temperatures.[11] Further variable-temperature X-ray and variable-field NMR studies will be needed in order to distinguish between these two possibilities.

As mentioned above, MC also crystallizes in a second polymorphic form (the β form) that can be obtained by slow evapo-

(26) (a) Hexem, J. G.; Frey, M. H.; Opella, S. J. *J. Chem. Phys.* **1982**, 77, 3847. (b) Olivieri, A. C.; Frydman, L.; Diaz, L. E. *J. Magn. Reson.* **1987**, 75, 50.

(27) (a) Suwelack, D.; Rothwell, W. P.; Waugh, J. S. *J. Chem. Phys.* **1980**, 73, 2559. (b) Schmidt, A.; Vega, S. *J. Chem. Phys.* **1987**, 87, 6895.

(28) Frydman, L.; Olivieri, A. C.; Diaz, L. E.; Frydman, B.; Schmidt, A.; Vega, S. *Mol. Phys.* In press.

¹³C NMR Study of "Arene-Olefin" Valence Tautomerism

J. Am. Chem. Soc., Vol. 112, No. 18, 1990 6475

ration at 0 °C from a methanol solution or, as was observed during the course of the present study, by heating α-MC above 75 °C. Figure 4 shows a set of representative ¹³C CPMAS NMR spectra of β-MC recorded at different temperatures. The MC molecules in this form crystallize with $Z = 8$ in space group $C2/c$, and there is therefore only one molecule per asymmetric unit.[11] The room temperature shift of the C1/C6 resonance is 65.3 ppm, about 2 ppm less than the C1/C6 solution chemical shift. As the temperature is lowered, the C1/C6 resonance experiences a considerable upfield shift, which can also be noted in the resonance frequency of C11. Table II summarizes the changes that are observed in the chemical shifts of the bridgehead carbon resonances of this form.

Discussion

1,6-Methano[10]annulenes offer a good model for studying the mechanism of solid-state reactions, not only due to the availability of a great variety of derivatives but also due to the revealing X-ray data that have been collected over the last years, mainly by the groups of Simonetta and Dunitz. It is therefore convenient to analyze, in the light of these diffraction studies, the chemical meaning of the solid-state NMR results presented in Tables I and II. Undoubtely, the differences in the free energies of the aromatic and olefinic tautomers of the DIM and the MC molecules are small enough to be overpowered by the packing forces that are present in the crystals. Nevertheless, the original question remains, namely, are the changes observed in the chemical shifts of the C1/C6 resonances at different temperatures reflecting a change in the equilibrium constant of a fast-exchange tautomerism, or are they reflecting the different degrees of advancement of the I ⇌ II process along a flat, asymmetric, energy profile? Although a definitive answer to this question will have to wait for subsequent analyses at very low temperatures, it is conceivable that both mechanisms are involved in the observed changes. Hints in this sense stem from the need to merge into a single picture the continuous change in the C1/C6 chemical shifts, which strongly suggests a solid-state exchange process proceeding fast on the NMR time scale, and the significant changes observed by X-ray diffraction in the geometry of the molecules of β-MC as the temperature is lowered.[11] Since it is very likely that the thermodynamic parameters of the valence tautomerism I ⇌ II are controlled by the geometry of the atoms at each temperature, the changes that CPMAS NMR monitors are probably reflecting both the changes in the equilibrium constant of the tautomerism and the changes in the energy profiles of the I ⇌ II process at each temperature.

Notwithstanding these considerations, the determination of the thermodynamic parameters that control the changes observed by ¹³C CPMAS NMR might be of considerable interest for the pursuit of further work on the nature of valence tautomerisms of the present kind. Although the low-temperature limiting values of the C1/C6 carbons in I and II (δ_I and δ_{II}) could not be reached in the present study, it is still possible to obtain a good approximation to the value of the equilibrium constant K of the tautomerism at each temperature. To do so, it is convenient to work with the chemical shift of the C1/C6 carbons ($\delta_{1,6}$) corrected by the contribution of the substituents at C11 (Δ_{11}). Assuming that this correction is the same for the aromatic and for the olefinic tautomers, its value can be obtained from standard NMR tables ($\Delta_{11} = 18.8$ ppm for R = R' = CH₃; $\Delta_{11} = 11.8$ ppm for R = CH₃, R' = CN)[29] and allows the corrected C1/C6 chemical shifts to be expressed as

$$\delta^*_{1,6} = \delta_{1,6} - \Delta_{11} = p_I\delta^*_I + p_{II}\delta^*_{II} \qquad (1)$$

where p_I and p_{II} are the relative populations of I and II at each temperature and δ^*_I and δ^*_{II} are the chemical shifts of the C1/C6 carbons in the aromatic and olefinic tautomers corrected by Δ_{11}.
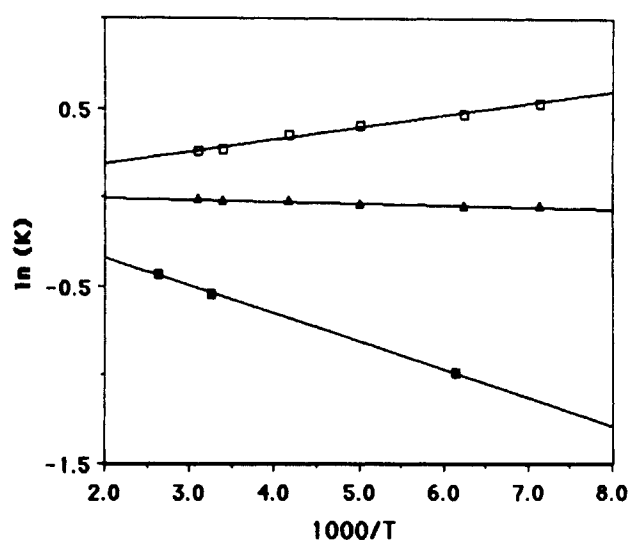
(29) Abraham, R. J.; Loftus, P. *Proton and Carbon-13 NMR Spectroscopy*; Wiley: New York, 1985.

Figure 5. Plot of the log of the equilibrium constant vs inverse temperature for the two molecules of solid DIM (▲, molecule A; □, molecule B) and for DIM in solution (■). In all cases, the correlation coefficients of the fittings ranged between 0.95 and 1.0.
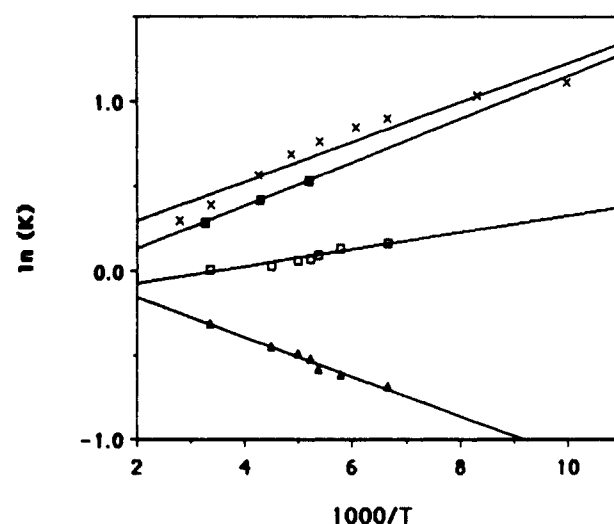

Figure 6. Plot of the log of the equilibrium constant vs inverse temperature for the two molecules of the α-MC polymorph (▲, molecule A; □, molecule B), for the β-MC polymorph (×), and for MC in solution (■). In all cases, the correlation coefficients of the fittings ranged between 0.95 and 1.0.

Table III. Thermodynamic Parameters for the Valence Tautomerism of DIM and MC in Solution and in the Solid State[a]

molecule	ΔH, cal/mol	ΔS, eu
DIM, solution	320 ± 20	0.0 ± 0.1
DIM, molecule A	20 ± 30	0.0 ± 0.1
DIM, molecule B	−140 ± 20	0.1 ± 0.1
MC, solution	−250 ± 20	−0.2 ± 0.1
α-MC, molecule A	240 ± 20	0.2 ± 0.1
α-MC, molecule B	−100 ± 30	−0.4 ± 0.1
β-MC	−230 ± 30	0.1 ± 0.1

[a] From the equation $K = e^{-\Delta G/RT} = e^{\Delta S/R}e^{-\Delta H/RT}$

Defining the equilibrium constant K of the process as $K = p_{II}/p_I$, the free energy ΔG of the equilibrium can be obtained from eq 1 as

$$-\frac{\Delta G}{RT} = \ln K = \ln\left(\frac{\delta^*_{1,6} - \delta^*_I}{\delta^*_{II} - \delta^*_{1,6}}\right) \qquad (2)$$

A good approximation to the value of δ^*_I can be obtained from the $\delta_{1,6}$ of 11,11-difluoro-1,6-methano[10]annulene (118.0 ppm), a compound that both X-ray and solution NMR techniques
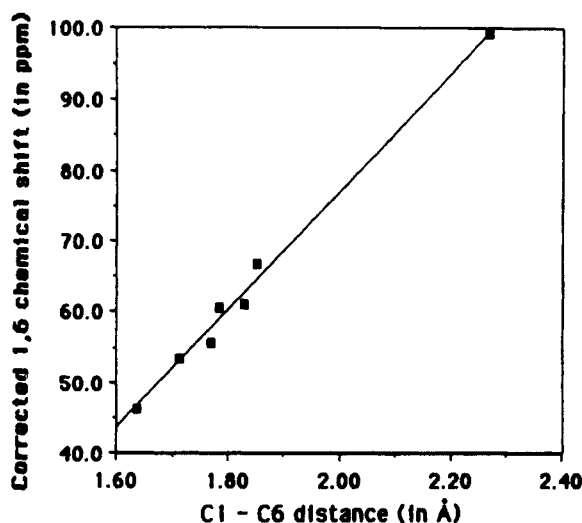
Figure 7. Correlation between the C1–C6 distance and the corrected chemical shift in DIM, α-MC, and β-MC at room temperature, β-MC at –100 °C, and the difluoro derivative. The solid line is the best fit of the data and yields $\delta^*_{1,6} = -90 + 83.5d_{1,6}$ ppm with a correlation coefficient $r = 1.0$.

identify as aromatic.[7,9] Although a model compound for obtaining δ^*_{II} is not available, an estimation of $(\delta^*_I + \delta^*_{II})/2$ can be made from the high-temperature limiting value of the C1/C6 resonance of the A molecules in DIM, whose chemical shift is almost temperature independent. This yields the extreme values of the two chemical shifts ($\delta^*_I = 99.2$ ppm, $\delta^*_{II} = 22.4$ ppm) and, with the aid of eq 2, the van't Hoff plots for MC and DIM that are shown in Figures 5 and 6. A summary of the parameters involved in the processes is shown in Table III.

During the course of the X-ray studies on 1,6-methano[10]-annulenes, different approaches have been proposed to correlate the bond lengths and the bond angles with the aromatic character of the molecules.[13] Although in all cases the structural parameter of choice was obvious (the C1–C6 distance), the parameter that had to define the electronic status of the ring was less evident. The corrected chemical shifts $\delta^*_{1,6}$ defined above appear as a convenient parameter for probing the aromaticity of the molecules. Figure 7 shows the correlation between the C1–C6 distance and $\delta^*_{1,6}$ for the molecules of DIM, α-MC, and β-MC at room temperature as well as for the β-MC molecule at –100 °C. The difluoro derivative was also included for the purpose of comparison. As can be seen, there is a good correlation between the results given by the two methods.

Conclusion

The present study is an additional example of the usefulness of solid-state NMR for the characterization of dynamic processes in the solid phase. By use of the ^{13}C CPMAS NMR technique it is possible to get a more complete picture of the results that were observed for MC and DIM in their solution NMR and X-ray diffraction analyses. The solid-state NMR results suggest that the process of valence tautomerism in 1,6-methano[10]annulenes is too complex to be characterized by only a single structural parameter. Moreover, the anomalous C1–C6 distances observed in the cases of the DIM and MC derivatives are probably reflecting the most stable geometry that allows the presence of a dynamic I $\rightleftharpoons$ II process rather than an extremely long C1–C6 bond in a more or less aromatic molecule.

Although the complete characterization of the energy potential profile for the I $\rightleftharpoons$ II process will have to wait for a future study, the data shown in Tables I and II may be useful for a better understanding of the geometry of 1,6-[methano10]annulenes. Indeed, if the changes in the configuration of the atoms in annulenes can be correlated with the changes in the equilibrium constants of the process as observed by NMR, it should be possible to obtain the geometry of the annulene and of the bisnorcaradiene tautomers. The solution, X-ray diffraction, and solid-state NMR results can also be used for obtaining an approximate idea of the mechanism of the I $\rightleftharpoons$ II process. Since the energies observed in the present study should be equal to the energies measured by solution NMR plus the contribution of intermolecular packing forces, it should be possible to propose a model according to which the molecules rearrange in the average potential field of the crystal in such a way that the changes in the potential packing energies calculated by theoretical methods reproduce the differences between the energies of the tautomers when measured by solution and by solid-state NMR. Moreover, the conclusions of such a study could also be compared with the results that can be obtained from a careful study of the anisotropic displacement parameters[30] in order to obtain a more complete picture of the effects that control the valence tautomerism of 1,6-methano[10]annulenes.

(30) Dunitz, J. D.; Maverick, E. F.; Trueblood, K. N. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 880.