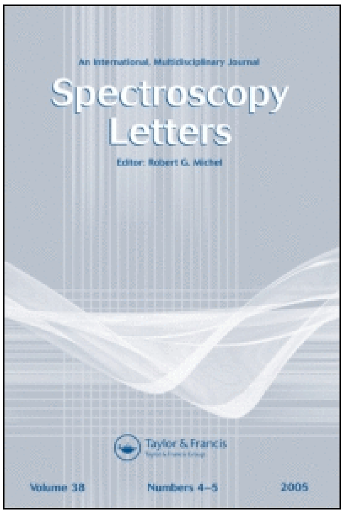


**Spectroscopy Letters**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

# Analysis of $^1$H and $^{13}$C{$^1$H} NMR Spectral Parameters and Geometries of Three Isomeric Diphenylbicyclo[2.2.1]Hept-5-Ene-2,3-Dicarboxylic Anhydrides

Mariitta Kokko[a]; Markku Mesilaakso[b]; Aarne Pajunen[c]
[a] Department of Chemistry, Laboratory of Organic Chemistry, University of Helsinki, Finland [b] Finnish Institute for Verification of the Chemical Weapons Convention, University of Helsinki, Finland [c] Department of Chemistry, Laboratory of Inorganic Chemistry, University of Helsinki, Finland

**To cite this Article** Kokko, Mariitta , Mesilaakso, Markku and Pajunen, Aarne(2000) 'Analysis of $^1$H and $^{13}$C{$^1$H} NMR Spectral Parameters and Geometries of Three Isomeric Diphenylbicyclo[2.2.1]Hept-5-Ene-2,3-Dicarboxylic Anhydrides', Spectroscopy Letters, 33: 5, 717 — 734
**To link to this Article: DOI:** 10.1080/00387010009350153
**URL:** http://dx.doi.org/10.1080/00387010009350153

SPECTROSCOPY LETTERS, 33(5), 717–734 (2000)

# ANALYSIS OF $^1$H AND $^{13}$C{$^1$H} NMR SPECTRAL PARAMETERS AND GEOMETRIES OF THREE ISOMERIC DIPHENYLBICYCLO[2.2.1]HEPT-5-ENE-2,3-DICARBOXYLIC ANHYDRIDES

**Keywords:** NMR; $^1$H NMR; $^{13}$C NMR; diphenylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydrides; geometry

Mariitta Kokko[a]*, Markku Mesilaakso[b] and Aarne Pajunen[c]

[a]Department of Chemistry, Laboratory of Organic Chemistry, P.O. Box 55, FIN-00014 University of Helsinki, Finland, [b]Finnish Institute for Verification of the Chemical Weapons Convention, P.O. Box 55, FIN-00014 University of Helsinki, Finland and [C]Department of Chemistry, Laboratory of Inorganic Chemistry, P.O. Box 55, FIN-00014 University of Helsinki, Finland.

---

*Author to whom correspondence should be addressed

## ABSTRACT

Diels-Alder adducts of 1,4-diphenyl-1,3-cyclopentadiene and maleic anhydride were investigated by recording the $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra of three isomeric diphenylbicyclo[2.2.1]hept-5-ene *endo* and *exo* 2,3-dianhydrides. The spectra were recorded in $CD_2Cl_2$ and analysed completely. The effect of the *endo* and *exo* configuration of the anhydride ring on the chemical shifts of the bridgehead phenyl protons is discussed. The ortho protons of the *exo* isomers resonate at higher field than those of the *endo* isomer, and the resonance pattern of the aromatic protons is narrower in the *exo* than the *endo* anhydride. The aromatic regions of the spectra are compared with the same regions of the $^{1}H$ NMR spectra of the earlier investigated addition products of 1,4-di-*p*-tolyl-1,3-cyclopentadiene and 1-phenyl-4-*p*-tolyl-1,3-cyclopentadiene with maleic anhydride. Chemical shifts of the bridge protons are explained on the basis of X-ray data of the compounds and MacroModel calculations on the minimum energy conformations.

## INTRODUCTION

Substituent effects on the $^{1}H$ and $^{13}C$ chemical shifts as well as the effects of molecular geometry on spin-spin coupling constants have been discussed for a variety of bicyclo[2.2.1]heptene (norbornene) derivatives.[1-9] Fewer studies have dealt with aryl-substituted norbornenes.[10-13] Whereas, inductive and mesomeric substituent effects are transmitted through chemical bonds, interaction of anisotropic groups such as: carbonyls, carbon-carbon double bonds, and phenyls occurs through space.[14] On the basis of their examination of a number of adducts of tetraphenylcyclopentadienone with different dienophiles (e.g., maleic anhydride, cyclohexene, norbornene), Coxon and Battiste[15] "cautiously" suggested the rule that in an *exo* adduct the protons of the bridgehead phenyls appear as a downfield singlet (at 60 MHz), while the protons of the phenyls at double bond form an upfield multiplet. In *endo* adducts the proton resonances of both types of phenyls usually appear as multiplets. Warrener with his co-workers[16] showed later that the *endo/exo* stereochemistry of the addition products of tetraphenylcyclopenta-dienone or phencyclone and various cyclobutenes cannot be predicted according to the rule of Coxon and Battiste because there is no singlet resonance of aromatic protons in the 80 MHz spectra of the *exo* adducts. Their dienophiles consisted of exceptional four-membered rings which can be expected to have less steric interactions with bridgehead phenyls. Hindered rotation of the bridgehead phenyls was later demonstrated by LaPlanche *et al.*[17,18] using 200 MHz $^1$H NMR spectra of phencyclone - norbornadiene adducts.

Earlier inspection[13] of 60 MHz $^1$H NMR spectra of diarylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydrides (**1** - **9**) in $CDCl_3$ revealed a complex multiplet for the *endo* anhydrides and a singlet-like resonance for the *exo* anhydrides at the aromatic regions (unpublished results).

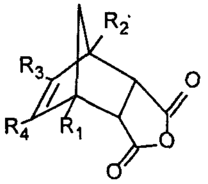
In the present study, we prepared 1,4-diphenylbicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboxylic anhydride (**10**), 1,5-diphenylbicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboxylic anhydride (**11**), and 1,5-diphenylbicyclo[2.2.1]hept-

5-ene-*exo*-2,*exo*-3-dicarboxylic anhydride (**12**), and investigated the effects of the substituents and molecular geometries on spectral parameters. A complete analysis of the 400 MHz $^1$H NMR spectra makes it possible to explain why the signals of the C-1 phenyl protons of the *exo* adducts at 60 MHz looked like a singlet in earlier investigations. Molecular modelling and X-ray data confirm the results. The $^{13}$C{$^1$H} NMR spectra of the three anhydrides were also analysed completely for the first time.

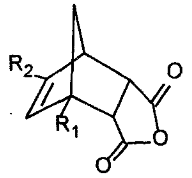
## EXPERIMENTAL

The synthesis and structural determinations of **1** - **9** have been described earlier.[13] Compounds **10** - **12** were synthesised according to Leppänen[10] and the structures were verified on the basis of melting points and MS, IR and NMR spectra.

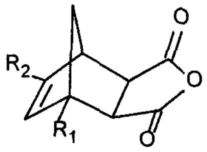
For the present studies, 33 mg of **10**, 42 mg of **11** and 28 mg of **12** were separately dissolved in 0.8 ml of $CD_2Cl_2$ (Acros, 99.6%-D). TMS (Sigma) served as internal chemical shift reference ($\delta_H$=$\delta_C$=0.00 ppm). The spectra were recorded on a Bruker AMX-400 at +30 °C. The 400 MHz $^1$H NMR spectra were recorded with 32 transients, a 6.4 μs pulse duration (flip angle 45°), a 22.9 s repetition time, a 4717.0 Hz spectral width, and 64k and 128k data points in the time and frequency domains, respectively. For the iterative computer analysis the data were resolution enhanced by gaussian multiplication. The $^1$H NMR spectral parameters ($\delta_H$, $^nJ_{H,H}$) were analysed with PERCH NMR software.[19]



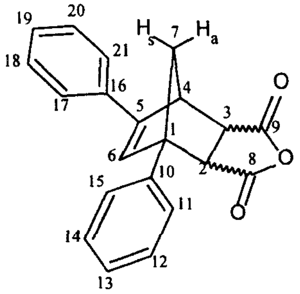
1: $R_1 = R_2 = R_3 = R_4 = C_6H_5$
2: $R_1 = C_6H_5$; $R_2 = C_6H_4CH_3$
$R_3 = R_4 = H$
7: $R_1 = R_2 = C_6H_4CH_3$
$R_3 = R_4 = H$
10: $R_1 = R_2 = C_6H_5$
$R_3 = R_4 = H$



3: $R_1 = C_6H_5$; $R_2 = C_6H_4CH_3$
5: $R_1 = C_6H_4CH_3$; $R_2 = C_6H_5$
8: $R_1 = R_2 = C_6H_4CH_3$
11: $R_1 = R_2 = C_6H_5$



4: $R_1 = C_6H_5$; $R_2 = C_6H_4CH_3$
6: $R_1 = C_6H_4CH_3$; $R_2 = C_6H_5$
9: $R_1 = R_2 = C_6H_4CH_3$
12: $R_1 = R_2 = C_6H_5$



The 100 MHz $^{13}$C{$^1$H} NMR spectra were recorded with 210-866 transients, a 3.8 μs pulse duration (flip angle 45°), a 3.6 s repetition time, a 23809.5 Hz spectral width, and 64k and 128k data points in the time and frequency domains, respectively. Exponential multiplication was applied using a 0.50 Hz line broadening factor. The accuracy of the determined chemical shifts is better than the digital resolution owing to the interpolation of the peak top frequencies by the spectrometer software. The $^1$H and $^{13}$C resonance assignments were confirmed with the aid of COSY[20a] and C,H-COSY spectra obtained with decoupling of proton-proton couplings in F1-dimension (optimised: 142 Hz) and long-range

C,H-COSY (optimised: 10 Hz).[20b] Molecular mechanics calculations were made with a MacroModel® interactive molecular modelling system.[21]

## RESULTS AND DISCUSSION

### Geometries of Compounds **10** - **12**

Except for the orientation of the anhydride ring, the greatest difference in the geometries of compounds **10** - **12** determined by molecular mechanics is the orientation of the phenyls at the bridgeheads (C-1 and C-4). The minimum energy dihedral angles between the phenyl rings and the bridge are -11° in compound **10** and -12° in compound **11**; in the *exo* compound **12** the corresponding angle is -1°. The same dihedral angles determined by X-ray diffraction are -17° in **11** and -5° in **12**.[22]

Even though the phenyls at C-1 and C-4 in the *endo* and *exo* isomers rotate, some steric repulsion exists between the ortho protons of the phenyl at C-1 and one carbonyl group, especially in the *exo* compound **12**. According to MacroModel calculations, the rotational barrier of the bridgehead phenyl is 29 kJ/mol (dihedral angle 75°) in the *exo* compound **12** and 4 kJ/mol and 8 kJ/mol (dihedral angles 75° and 160°, respectively) in the *endo* compounds **10** and **11**.

### $^1$H Chemical Shifts and Coupling Constants of Aliphatic Protons

The $^1$H chemical shifts and coupling constants of compounds **10** - **12** are presented in Table 1. Proton H-7a resonates at higher field than H-7s in the

TABLE 1

$^1$H NMR Spectral Parameters (δ[ppm], TMS=0.0 ppm, J[Hz])a) of **10**, **11** and **12** in $CD_2Cl_2$.

| | **10** | **11** | **12** |
|---|---|---|---|
| δ(H-2) | 4.065 | 3.963 | 3.439 |
| δ(H-3) | 4.065 | 4.000 | 3.394 |
| δ(H-4) | | 4.099 | 3.981 |
| δ(H-5) | 6.637 | | |
| δ(H-6) | 6.637 | 6.717 | 6.666 |
| δ(H-7syn) | 2.307 | 2.244 | 2.216 |
| δ(H-7anti) | 2.451 | 2.170 | 2.070 |
| δ(H-11, 15) | 7.572 | 7.598 | 7.406 |
| δ(H-12, 14) | 7.454 | 7.456 | 7.449 |
| δ(H-13) | 7.373 | 7.372 | 7.379 |
| δ(H-17, 21) | 7.572 | 7.508 | 7.511 |
| δ(H-18, 20) | 7.454 | 7.368 | 7.396 |
| δ(H-19) | 7.373 | 7.316 | 7.329 |
| J(H-2, H-3) | | 8.3 | 7.4 |
| J(H-2, H-7syn) | | | 1.6 |
| J(H-3, H-4) | | 4.7 | 1.1 |
| J(H-3, H-6) | | 0.4 | |
| J(H-3, H-7syn) | | | 1.6 |
| J(H-4, H-6) | | 1.3 | 1.2 |
| J(H-4, H-7anti) | | 1.5 | 1.6 |
| J(H-4, H-7syn) | | 1.7 | 1.7 |
| J(H-5, H-7anti) | 0.9 | | |
| J(H-5, H-7syn) | ~0.3[b] | | |
| J(H-6, H-7anti) | 0.9 | 0.8 | 0.9 |
| J(H-6, H-7syn) | ~0.3[b] | 0.3 | ~0.3[b] |
| J(H-7anti, H-7syn) | -9.0 | -9.0 | -10.1 |
| J(H-11, H-12) | 7.87 | 7.85 | 7.79 |
| J(H-11, H-13) | 1.20 | 1.21 | 1.22 |
| J(H-11, H-14) | 0.58 | 0.58 | 0.60 |
| J(H-11, H-15) | 2.09 | 2.11 | 2.03 |
| J(H-12, H-13) | 7.46 | 7.46 | 7.47 |
| J(H-12, H-14) | 1.48 | 1.47 | 1.46 |
| J(H-17, H-18) | 7.87 | 7.89 | 7.86 |
| J(H-17, H-19) | 1.20 | 1.20 | 1.21 |
| J(H-17,H-20) | 0.58 | 0.60 | 0.61 |
| J(H-17, H-21) | 2.09 | 2.01 | 1.98 |
| J(H-18, H-19) | 7.46 | 7.45 | 7.44 |
| J(H-18, H-20) | 1.48 | 1.44 | 1.45 |

a) The error in the chemical shifts is less than 0.001 ppm and in the coupling constants determined from the aromatic rings less than 0.01 Hz. In other couplings it is less than 0.1 Hz. b) Does not show splitting, i.e. the coupling is estimated from the linewidth.

unsubstituted bicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboxylic anhydride ($\Delta\delta \sim 0.19$ ppm) and in the corresponding *exo* anhydride ($\Delta\delta \sim 0.22$ ppm).[1,8,23] This is a common feature in norbornene derivatives when no anisotropic substituents are present.[24a] In the *endo* compound **10** the chemical shifts of H-7a and H-7s are 2.451 ppm and 2.307 ppm, respectively ($\Delta\delta = -0.144$ ppm). This exceptional order of the resonances was confirmed with NOESY, which revealed the spatial proximity of H-7a to H-2 and H-3. Coupling constants of H-5/H-6 with H-7a (0.9 Hz) and H-7s (0.3 Hz) further confirmed the assignment. The order of the chemical shifts of H-7a and H-7s in compounds **11** and **12** is the same as that in the unsubstituted anhydrides.

The differences in the chemical shifts of H-7a and H-7s can be explained by the geometries of the molecules. The C-1 and C-4 phenyls of **10** deshield H-7a more than H-7s because the aromatic rings are turned towards H-7a in their minimum conformation. Compound 11 does not have a phenyl ring at C-4, but still the deshielding effect of the aromatic ring[24b] can be seen: the chemical shift difference of H-7a and H-7s is 0.074 ppm. In **12** the aromatic ring at C-1 in its minimum energy conformation is almost equidistant from the bridge protons and the difference in the chemical shifts of H-7a and H-7s is 0.146 ppm.

The *endo/exo* configuration of norbornene derivatives can be determined in a number of ways. For example, the anisotropic double bond shifts the signals of the *exo* protons downfield and those of the *endo* protons upfield,[7,8] and the protons H-2 and H-3 resonate clearly downfield in **10** and **11** compared with **12**. Furthermore, the vicinal coupling constants between H-3 and H-4 are in good agreement with the Karplus curve: 4.7 Hz in **11** (X-ray dihedral angle 39°) and 1.1 Hz in **12** (dihedral angle 69°). An additional characteristic feature of the *exo* compound **12** is the W-path coupling of H-7s with H-2 and H-3 (both 1.6 Hz). Other W-path couplings are found between H-4 and H-6 in **11** and **12** (1.3 and 1.2 Hz, respectively).

## $^1$H Chemical Shifts of Aromatic and Olefinic Protons

The C-5 phenyl protons in compounds **10**, **11** and **12** form an AA'MM'X spin system, while the C-1 phenyl protons in **12** are an AA'DD'K system. Because of the symmetry in **10** the two spin systems are identical and overlap exactly; in **11** and **12** they overlap partly (Fig. 1). The aromatic protons are coupled only with the other protons in the same aromatic ring. The chemical shifts of the C-1 phenyl protons in **11** are similar to those in **10**, but the protons of the phenyl at C-5 resonate at higher field than the protons of the phenyl at C-1 (Table 1). In **12** the phenyl multiplets overlap each other much more and the resonances lie in a narrower region than in **10** and **11**. Owing to the orientation of the anhydride ring, the carbonyl group anisotropy affects the ortho protons of the phenyl at C-1 differently in *exo* and *endo* anhydrides; the chemical shifts of the ortho protons H-11 and H-15 in **12** move considerably (0.192 ppm) upfield. The chemical shifts

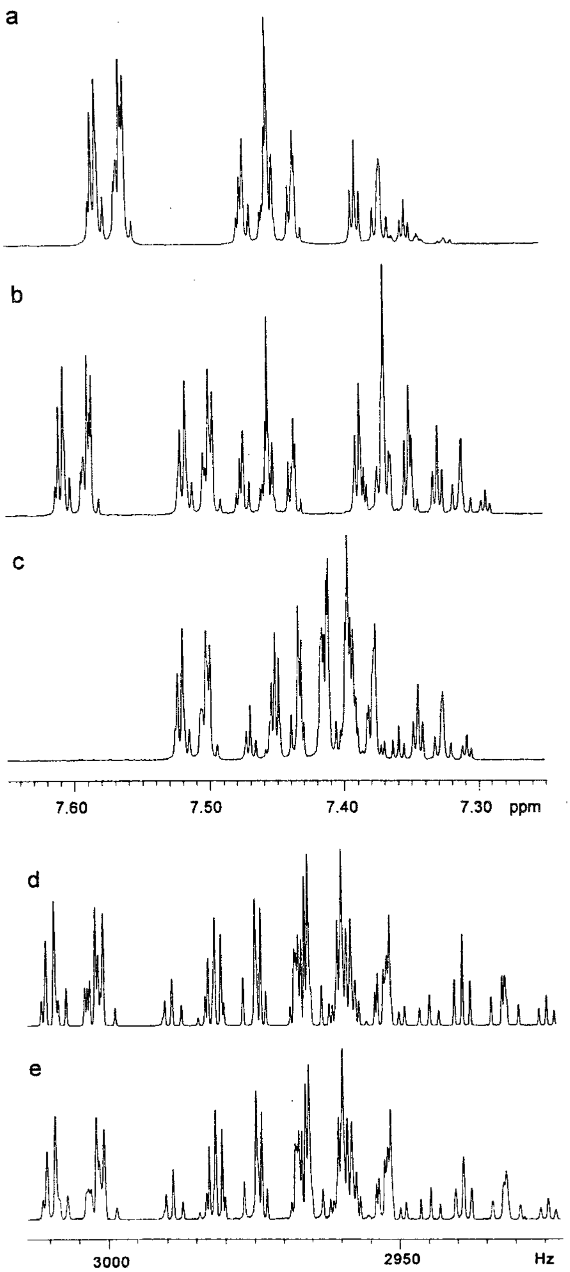


FIG. 1. The aromatic regions of 400 MHz $^1$H NMR spectra of a) **10**, b) **11**, c) **12**, d) **12** calculated, and e) **12** experimental.

of the C-1 phenyl protons are within 0.070 ppm in **12**, 0.225 ppm in **11**, and 0.199 ppm in **10**, which explains why a singlet-like resonance was observed for *exo* compounds in earlier investigations.[13,15]

The same "singlet" and "multiplet" resonances can be seen in the simulated 60 MHz $^1$H NMR spectra (line width 0.6 Hz; parameters from Table 1) of compounds **11** and **12** (Fig. 2). For comparison the aromatic regions of the 60 MHz $^1$H NMR spectra of aryl-substituted bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydrides **1** - **9** are shown in Fig. 3. Spectra of the *endo* compounds (**1, 2, 3, 5, 7, 8**) display multiplets, while the *exo* compounds (**4, 6, 9**) show singlet-like resonances of the C-1 phenyl protons together with a multiplet of the C -5 phenyl protons. Comparison of the *exo* compounds **9** and **12** shows that the aromatic tolyl protons resonate at higher field than the phenyl protons. The singlet-like resonance of the *exo* compound **6** occurs upfield of the other aromatic resonances and has the same chemical shift as the singlet-like resonance of **9**, leading to the conclusion that a tolyl group lies at C-1 and a phenyl group at C-5. Likewise, in the *exo* compound **4** there must be a phenyl at C-1 and a tolyl at C-5 because the singlet-like resonance appears downfield from the other aromatic signals and at the same frequency as the singlet-like resonance of **12**.

### $^{13}$C{$^1$H} NMR Spectra

The $^{13}$C chemical shifts of compounds **10** - **12** are presented in Table 2. The *exo* anhydride ring shifts the $^{13}$C resonance of C-7 upfield in **12** compared with

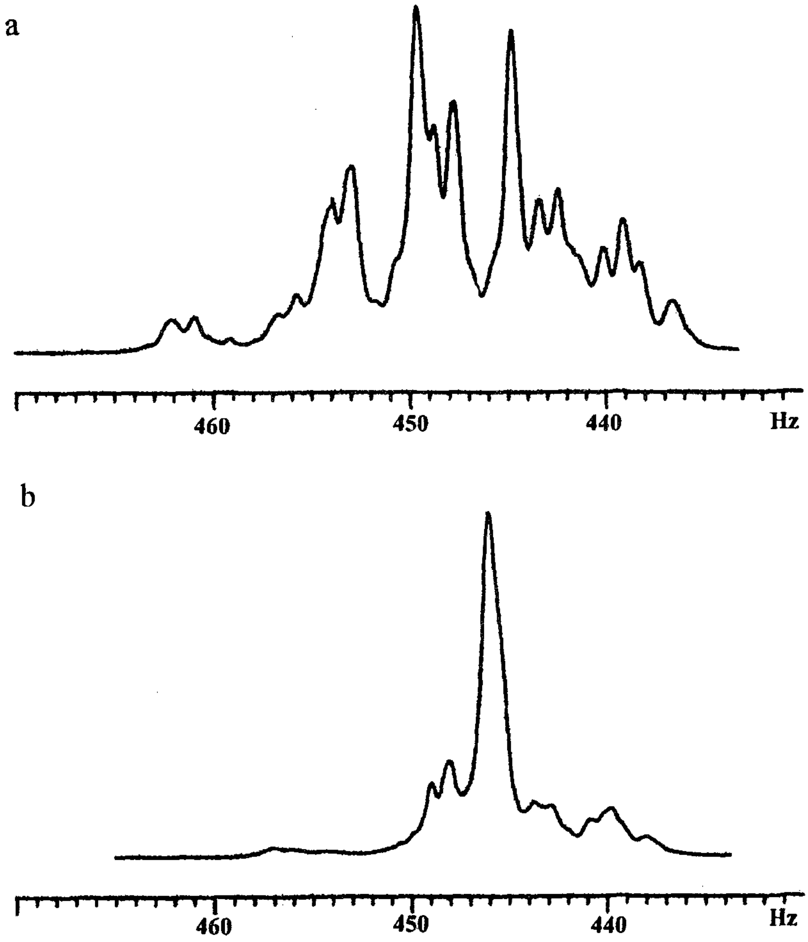


FIG. 2. The simulated aromatic regions of 60 MHz $^1$H NMR spectra of a) **11** and b) **12**. The simulations were done by using the spectral parameters obtained in this work.

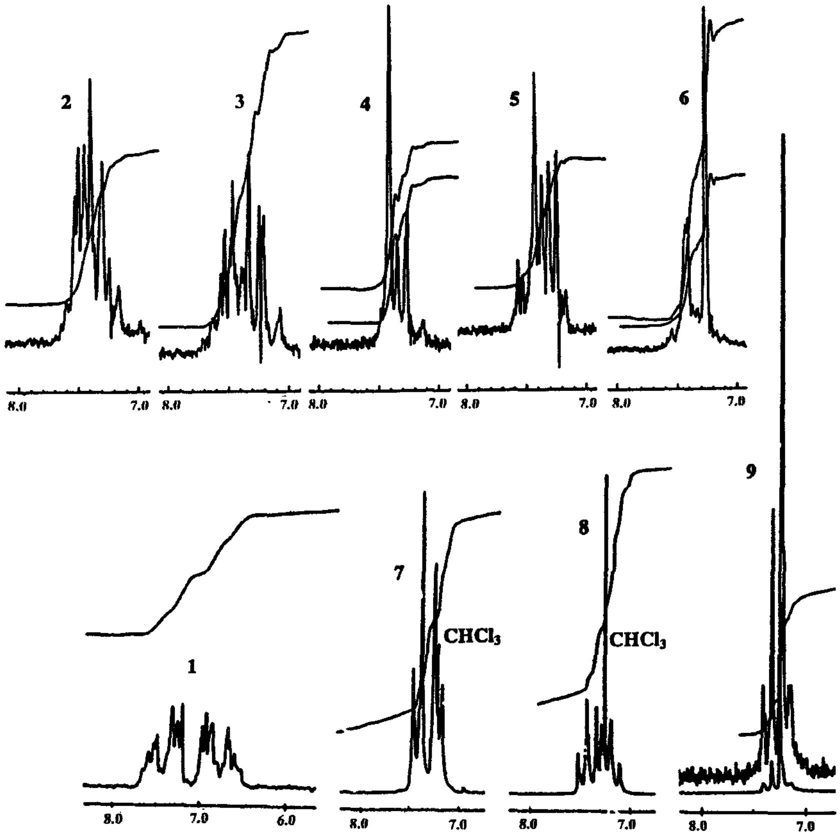


FIG. 3. The aromatic regions of the 60 MHz $^{1}$H NMR spectra of aryl-substituted bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydrides **1** - **9**.

TABLE 2

$^{13}C$ Chemical Shifts [a] (vs. TMS=0.0 ppm) of **10**, **11** and **12** in $CD_2Cl_2$.

| | **10** | **11** | **12** |
|---|---|---|---|
| δ(C-1) | 62.43 | 63.51 | 64.30 |
| δ(C-2) | 53.59 | 52.98 | 55.23 |
| δ(C-3) | 53.59 | 49.81 | 51.34 |
| δ(C-4) | 62.43 | 47.84 | 48.28 |
| δ(C-5) | 139.05 | 148.81 | 150.30 |
| δ(C-6) | 139.05 | 130.22 | 134.89 |
| δ(C-7) | 64.51 | 58.60 | 45.65 |
| δ(C-8) | 170.48 | 171.06 / 170.80 | 169.01 |
| δ(C-9) | 170.48 | 170.80 / 171.06 | 171.85 |
| δ(C-10) | 138.69 | 139.26 | 137.57 |
| δ(C-11, 15) | 127.41 | 127.49 | 127.54 |
| δ(C-12, 14) | 129.20 | 129.14 | 128.98 |
| δ(C-13) | 128.17 | 128.06 | 128.04 |
| δ(C-16) | 138.69 | 133.34 | 133.34 |
| δ(C-17, 21) | 127.41 | 126.23 | 125.59 |
| δ(C-18, 20) | 129.20 | 129.01 | 129.29 |
| δ(C-19) | 128.17 | 129.10 | 129.00 |

a) The error in the chemical shifts is less than 0.01 ppm.

the *endo* compounds **10** and **11** (Δδ = 18.66 ppm and 12.95 ppm, respectively). In all compounds, carbons C-5 and C-6 could be distinguished from the aromatic carbons through their correlation with H-7a. Carbons C-5 and C-6 also resonate upfield in **11** relative to **12**. The influence of the anhydride ring is greater on C-6 than on aryl-substituted C-5.

The downfield shift caused by the aromatic substituent is larger in position 2 (β-effect) than in position 3 (γ-effect), and in compounds **11** and **12**, therefore, C-2 resonates at a lower field than C-3. Although H-2 and H-3 in **11** resonate fairly close to each other, the chemical shifts of C-2 and C-3 could be assigned: C-2 and C-3 both correlate with H-7s, but C-2 correlates in addition with H-4. The $^{13}$C shifts of the carbonyl carbons C-8 and C-9 could not be assigned in **11**. The dihedral angle H-4–C-4–C-3–C-9 in **11** is 88°, which may be one reason for the missing correlation between C-9 and H-4. The corresponding dihedral angle in **12** is 49°; the carbonyl carbons C-8 and C-9 were distinguishable from one another because only C-9 correlates with H-4.

## CONCLUSION

Although the bridgehead phenyl rotates, the steric interactions are larger in the *exo* anhydride **12** than in the *endo* anhydrides **10** and **11**. The ortho protons of the C-1 phenyl are shifted upfield in **12**, with the result that the protons of the C-1 phenyl resonate in a considerably narrower range than the corresponding protons in **10** and **11**. This observation explains the earlier results obtained with low-field spectrometers.

The conformations of the C-1 phenyls of **11** and **12** in solid state provide an explanation for the chemical shifts of H-7a and H-7s in liquid state. On this basis the solid state and minimum energy liquid state conformations would appear to be similar.

## REFERENCES

1. Kamezawa N., Sakashita K. and Hayamizu K. Nuclear Magnetic Resonance Studies of 5,6-Dicarboxy-2-norbornene Derivatives. Org. Magn. Reson. 1969; 1: 405-414.

2. Abraham R. J. and Fisher J. Substituent Chemical Shifts in NMR. 1 - Proton Resonance Spectra and Geometries of Norbornene, Norbornane and Adamantane. Magn. Res. Chem. 1985; 23: 856-861.

3. Abraham R. J. and Fisher J. Substituent Chemical Shifts in NMR. 3 - Carbonitrile SCS in Rigid Molecules. Magn. Res. Chem. 1986; 24: 451-459.

4. Fisher J. and Gradwell M. J. Complete Assignment of the $^1$H and $^{13}$C NMR Spectra of Norbornene Derivatives. Magn. Res. Chem. 1991; 29: 1068-1074.

5. Cavasotto C. N., Giribet C. G., Ruiz de Azúa M. C. and Contreras R. H. *Exo-Exo* and *Endo-Endo* Vicinal Proton Spin-Spin Coupling Constants in Norbornane and Norbornene. An IPPP-CLOPPA Analysis. J. Comput. Chem. 1991; 12: 141-146.

6. Anet F. A. L., Lee H. H. and Sudmeier J. L. Coupling Constants in the Nuclear Magnetic Resonance Spectra of *endo-* and *exo*-Norbornene Derivatives. J. Am. Chem. Soc. 1967; 89: 4431-4434.

7. Fraser R. S. The Establishment of Configuration in Diels-Alder Adducts by N.M.R. Spectroscopy. Can. J. Chem. 1962; 40: 78-84.

8. Marchand A. P. and Rose J. E. On the Question of Bridge-Proton Absorptions in the Nuclear Magnetic Resonance Spectra of Norbornene and Related Systems. J. Am. Chem. Soc. 1968; 90: 3724-3731.

9. Stothers J. B., Tan C. T. and Teo C. $^{13}$C Nuclear Magnetic Resonance Studies. 55. A Comparison of the Stereochemical Dependence of $\gamma$- and $\delta$-Substituent Effects on $^{13}$C Shielding in Several Norbornanols and Norbornenols. Can. J. Chem. 1976; 54: 1211-1221.

10. Leppänen K. Über die Diels-Alder-Addukte von 1,4-Diphenylcyclopentadien und Maleinsäureanhydrid. *Endo-Exo*-Isomerisation. *Ann. Acad. Sci. Fenn. A* 1965; II 131: 1-50.

11. Prinzbach H. and Thyes M. Phenylsubstituirte Quadricyclanester, Synthese, Thermolyse, Cycloaddition. Chem. Ber. 1971; 104: 2489-2516.

12. Beugelmans-Verrier M., Nicolas L., Gaudemer A. and Parello J. Interaction Entre un Groupement Carboxylique et un Groupement Aromatique, en Serie Norbornene, Etudiee par RMN du Carbone 13 et par Mesure du pKa. Tetrahedron Lett. 1976; 361-364.

13. Kokko M. The Diels-Alder Reactions of Some Arylcyclopentadienes with Maleic Anhydride. Ann. Acad. Sci. Fenn. A 1980; II 191: 1-84.

14. Friebolin H., *Basic One- and Two-Dimensional NMR Spectroscopy.* Weinheim: VCH Verlagsgesellschaft mbH 1993 (2nd. ed.): 45.

15. Coxon J. M. and Battiste M. A. Reaction of Tetraphenylcyclopentadienone with Cyclic Olefins: An NMR Probe of Adduct Stereochemistry. Tetrahedron 1976; 32: 2053-2056.

16. Warrener R. N., Tan R. Y. S. and Russel R. A. The Stereochemistry of the Adduct Derived from the Diels-Alder Addition of Cyclobutenes and Cyclopentadienones: A Caveat on Some Existing PMR Methods for the Assignment of Stereochemistry. Tetrahedron Lett. 1979; 2943-2946.

17. LaPlanche L. A., Xu Y., Benshafrut R., Rothchild R. andHarrison, Jr. E. A. NMR Studies of Hindered Rotation of Unsubstituted Bridgehead Phenyl Rings in the Phencyclone - Norbornadiene Adduct. Spectroscopy Letters 1993; 26: 79-101.

18. Xu Y., LaPlanche L. A. and Rothchild R. Assignment of $^{13}$C Resonances in the Phencyclone - Norbornadiene Adduct via 2D NMR. $^{13}$C Evidence for Hindered Rotation of Unsubstituted Bridgehead Phenyl Rings. Spectroscopy Letters 1993; 26: 179-196.

19. Laatikainen R. Automated Analysis of NMR Spectra. J. Magn. Reson. 1991; 92: 1-9.

20. Martin G. E. and Zektzer A. S. *Two-Dimensional NMR Methods for Establishing Molecular Connectivity. A Chemist's Guide to Experimental Selection, Performance, and Interpretation.* Weinheim: VCH Verlagsgesellschaft mbH 1988: a) 59, b) 201.

21. Still W. C., Mohamadi F., Richards N. G. J., Guida W. C., Lipton M., Liskamp R., Chang G., Hendrickson T., DeGunst F., Hasel W., *MacroModel® V3.1.* , Department of Chemistry, Columbia University, New York, NY.

22. Pajunen A. and Kokko M. 1,5-Diphenylbicyclo[2.2.1]hept-5-ene-*endo*-2,*endo*-3-dicarboxylic Anhydride and 1,5-Diphenylbicyclo[2.2.1]hept-5-ene-*exo-2,*exo-3-dicarboxylic Anhydride. Acta Cryst. 1998; C54: 1724-1727.

23. Kokko M. and Koskimies J. Configurational Assignments of 5-Norbornene-2,3-dicarboximide and N-Phenyl-5-norbornene-2,3-dicarboximide by One- and Two-Dimensional NMR Spectroscopy. Spectroscopy Letters 1995; 28: 347-358.

24. Günther H. *NMR Spectroscopy. Basic Principles, Concepts and Applications in Chemistry.* Chichester: John Wiley & Sons 1994 (2nd ed.): a) 83 and b) 85.

Date Received; December 30, 1999
Date Accepted; June 1, 2000