# Structure and Conformation of 1,4-Dihydrobenzene, 1,4-Dihydronaphthalene, and 9,10-Dihydroanthracene. A Theoretical Study

Kenny B. Lipkowitz* and Peter W. Rabideau*

*Department of Chemistry, Indiana-Purdue University at Indianapolis, Indianapolis, Indiana 46205*

Douglas J. Raber* and Linda E. Hardee

*Department of Chemistry, University of South Florida, Tampa, Florida 33620*

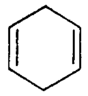
Paul v. R. Schleyer,* Alexander J. Kos, and Richard A. Kahn

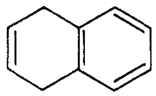
*Institut für Organische Chemie der Friedrich-Alexander-Universität, Erlangen-Nürnberg, D-8520 Erlangen, Federal Republic of Germany*

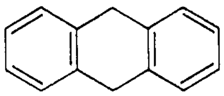
*Received May 27, 1981*

The title compounds have been studied by using both molecular mechanics (MMI and MM2) and molecular orbital [MINDO/3, MNDO, and ab initio (3-21G basis)] calculations. The optimum structure is found to be planar in each case, although the energy required for nonplanar distortion is small and decreases regularly with the degree of benzannulation. The large puckering amplitudes to be expected explain the experimentally observed behavior.

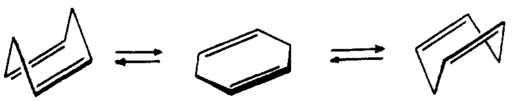
The shapes of 1,4-dihydrobenzene (1) and of its dihydronaphthalene and dihydroanthracene analogues (2 and 3) have long been a question to which chemists have sought a definitive answer.[1] Considerable recent interest has also been exhibited in substituted derivatives of 1–3 and in their biologically important heterocyclic analogues.[2] The structural similarity of 1–3 to biologically and medically important quinones[3] further underscores the need to understand fully the structures of the parent compounds.


1

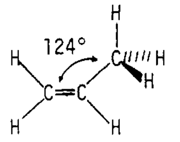

2

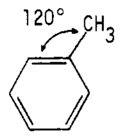

3

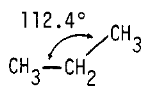
Do the preferred conformations of the 1,4-dihydro aromatic compounds correspond to planar structures (e.g., **1a**) or to pairs of equilibrating "boat" conformations (**1b**)?[1] We have now undertaken a careful computational study of 1–3.


1b $C_{2v}$ 1a $D_{2h}$ 1b $C_{2v}$

Some of the controversy regarding the conformation of dihydro aromatic compounds can be traced to the choice of the model upon which expectations are based. Consider first the question of angle strain. For a *planar* six-membered ring the sum of the interior angles must be 720° (i.e., the average bond angle in the ring must be 120°). Using 120° and 109.5° as the optimum angles at $sp^2$ and $sp^3$ centers, respectively, substantial angle strain would be expected for planar conformations of 1–3. This situation is reflected by the behavior of Dreiding models, which show a clear preference for nonplanarity. However, neither 109.5° nor 120° bond angles may be optimal. While toluene may be a good model for the aromatic derivative 3, a simple alkene such as propene with a $C{=}C{-}CH_3$ bond angle of 124°[4] is a much more appropriate model for the dihydrobenzene 1. Propane, with a C–C–C bond angle of 112.4°,[4] can be used to model the C–$CH_2$–C angle of 1–3.







Using the appropriate bond angles for toluene, propene, and propane as optimal, the sum of the interior angles in a model planar structure for 3 would be 705° [i.e., (4 × 120°) + (2 × 112.4°)], whereas the interior angles in the corresponding model planar structure for dihydrobenzene 1 would add up to 721° [i.e., (4 × 124°) + (2 × 112.4°)]. Consequently, planarity could be achieved in dihydroanthracene 3 only with some angle distortion (705° vs. 720°). In contrast, planar 1,4-dihydrobenzene (1) should have no angle deformation. The angle strain for planar dihydronaphthalene 2 would be intermediate, and the trend for angle strain would favor nonplanar structures in the order 3 > 2 > 1.

Torsional effects also are important. In the planar conformations of 1–3, the two hydrogens of each $CH_2$ group are symmetrically staggered with respect to the adjacent vinyl hydrogens or aryl ring. Propene and toluene again model the effects to be expected in 1–3. The preferred conformation of propene, with the vinyl hydrogen staggered between two hydrogens of the adjacent methyl group,[4] would favor a planar conformation for 1. Any distortion from planarity will therefore lead to unfavorable torsional (eclipsing) interactions. (Note that this effect is not incorporated into Dreiding models which only reflect angle strain.) On the other hand, toluene exhibits no

---

[1] For a critical review see P. W. Rabideau, *Acc. Chem. Res.*, 11, 141 (1978).

[2] (a) T. J. van Bergen, D. M. Hedstrand, W. H. Kruizinga, and R. M. Kellog, *J. Org. Chem.* 44, 4953 (1979); (b) Y. Tamura, C. Mukai, Y. Nishikawa, and M. Ikeda, *ibid.*, 44, 3296 (1979); (c) M. Sikirica, I. Vicković, V. Caplar, A. Sega, A. Lisini, F. Kajfež, and V. Sunjić, *ibid.*, 44, 4423 (1979).

[3] (a) J. Yadav, P. Corey, C.-T. Hsu, K. Perlman, and C. J. Sih, *Tetrahedron Lett.*, 22, 811 (1981); (b) K. A. Parker and J. Kallmerten, *J. Am. Chem. Soc.*, 102, 5881 (1980).

[4] (a) J. P. Lowe, *Prog. Phys. Org. Chem.*, 6, 1 (1968); (b) J. R. Lide, Jr., and D. Christensen, *J. Chem. Phys.*, 35, 1374 (1961); (c) J. R. Lide, Jr., *ibid.*, 33, 1514 (1960).

0022-3263/82/1947-1002$01.25/0

Table I. Structural Parameters for 1,4-Dihydrobenzene (1)

| bond length or angle | exptl[a] | STO-3G[b] | MMI | MINDO/3 | MNDO | 3-12G[c,d] |
|---|---|---|---|---|---|---|
| C(1)-C(2), Å | 1.496 | 1.522 | 1.502 | 1.498 | 1.506 | 1.514 |
| C(2)-C(3), Å | 1.334 | 1.309 | 1.338 | 1.347 | 1.347 | 1.322 |
| C(1)-H, Å | 1.114 | 1.093 | 1.098 | 1.121 | 1.116 | 1.089 |
| C(2)-H, Å | 1.103 | 1.084 | 1.096 | 1.106 | 1.092 | 1.101[d] |
| C(1)-C(2)-C(3), deg | 123.4 | 123.8 | 122.7 | 122.8 | 123.4 | 123.8 |
| C(2)-C(1)-C(6), deg | 113.3 | 112.3 | 114.7 | 113.8 | 113.2 | 112.3 |
| H-C(1)-H, deg | 103. | 106.0 | 111.0 | 102.5 | 106.3 | 106.2 |
| H-C(2)-C(3), deg | 123.4 | 120.4 | 119.4 | 121.0 | 121.2 | 119.8[d] |

[a] Reference 5a. [b] Reference 16; $E = -229.04362$ hartrees. (At the 4-31G level the energy for the identical geometry is reported as $-231.49636$ hartrees.) [c] $E = -230.54165$ hartrees. [d] Not fully optimized.

rotational preference;[4] hence, little torsional effect is predicted for **3**. Once again the dihydronaphthalene **2** should be intermediate. Torsional effects therefore should favor *planar* structures in the order **1** > **2** > **3**. The nonplanar forms of **1**–**3** should also be favored by their lower symmetry. This would contribute modestly (0.4 kcal/mol at 298 K) to the entropy term ($T\Delta S$).

Experimental data[1,5] for **1**–**3** are to some extent conflicting. A gas-phase electron-diffraction study of **1** favored a planar energy minimum.[5a] However, vibrational distortion from planarity results in *average* interatomic distances which are shorter than those in the planar structure; this apparently led to another conclusion[5b] (also based on an electron-diffraction study) that the optimum structure is nonplanar. Vibrational spectroscopy[5c–f] has also supported a planar structure for **1**. X-ray crystallography indicates[6] a nonplanar structure for 9,10-dihydroanthracene (**3**) with a dihedral angle between the two aromatic ring[7] planes of 145°, but such solid-state structures might be perturbed by crystal packing forces.[8] Studies of substituted derivatives of **1**–**3** by NMR and other methods have also led to conflicting structural conclusions[1] but may not be directly applicable to the parent compounds.

## Methods

Molecular mechanics calculations[9] were performed with Allinger's MMI[9b] and MM2[9d] programs, and the different nonplanar geometries were generated with the dihedral driver option. The C(2)–C(3)–C(4)–C(5) torsional angle[7] was varied, and this led to structures which remained close to $C_{2v}$ symmetry. Compounds **2** and **3** contain benzene rings for which MMI does not include all of the necessary parameters. Calculations on these compounds were carried out in two ways: (1) with MMPI; (2) by following Allinger's[9b] suggestion and defining a new "aromatic" sp$^2$ carbon atom. All parameters for this atom type are identical with those of olefinic sp$^2$ carbons except the optimum C=C bond length (1.397 Å) and the C=C force constant (8.0667 mdyn/Å). The two methods of calculation gave energy profiles which were virtually identical.

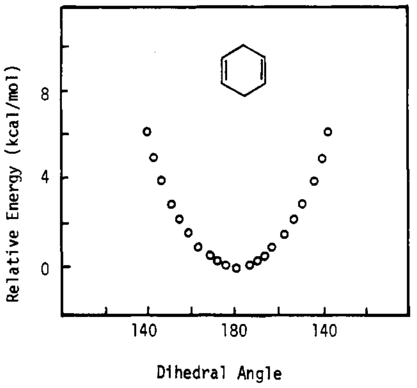


Figure 1. MMI energy profile of 1.

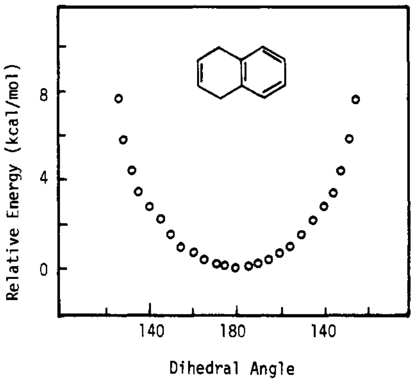


Figure 2. MMI energy profile of 2.

Molecular orbital calculations were carried out at all levels for **1** and at the MINDO/3 level[10a] for **3**. Our version of the MINDO/3 program was modified slightly to accommodate molecules such as **3** with more than 50 orbitals. The geometries were restricted to $C_{2v}$ symmetry (or $D_{2h}$ symmetry in the case of planar structures), and all bond lengths, bond angles, and torsional angles were optimized.

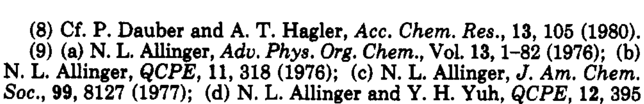
Ab initio calculations of **1** were performed with the Gaussian 76 series of programs[11] using a 3-21G basis set. All bond lengths, bond angles, and torsional angles were fully optimized with the exception of those pertaining to the four equivalent vinyl hydrogens. The geometries were restricted to $C_{2v}$ symmetry (or $D_{2h}$ symmetry for the planar structure).

---

[5] (a) G. Dallinga and L. H. Toneman, *J. Mol. Struct.*, 1, 117 (1967); (b) H. Oberhammer and S. H. Bauer, *J. Am. Chem. Soc.*, 91, 10 (1969); (c) J. Laane and R. C. Lord, *J. Mol. Spectrosc.*, 39, 340 (1971); (d) H. D. Stidham, *Spectrochim. Acta*, 21, 23 (1965); (e) B. J. Monostori and A. Weber, *J. Mol. Spectrosc.*, 12, 129 (1964); (f) H. Gerding and F. A. Haak, *Recl. Trav. Chim. Pays-Bas*, 68, 293 (1949).

[6] W. G. Ferrier and J. Iball, *Chem. Ind. (London)*, 1296 (1954).

[7] A description of 1–3 in terms of two intersecting planes (each having four or more atoms) is only an approximation in the absence of rigorous $C_{2v}$ symmetry, and the reported geometry is the average of two dihedral angles about a line joining the saturated carbon atoms (C-1 and C-4) as illustrated for 1.



[8] Cf. P. Dauber and A. T. Hagler, *Acc. Chem. Res.*, 13, 105 (1980).

[9] (a) N. L. Allinger, *Adv. Phys. Org. Chem.*, Vol. 13, 1–82 (1976); (b) N. L. Allinger, *QCPE*, 11, 318 (1976); (c) N. L. Allinger, *J. Am. Chem. Soc.*, 99, 8127 (1977); (d) N. L. Allinger and Y. H. Yuh, *QCPE*, 12, 395 (1980).

[10] (a) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, 97, 1285 (1975). (b) M. J. S. Dewar and W. Thiel, *ibid.*, 99, 4899, 4907 (1977).

[11] Gaussian 76: J. S. Binkley, R. A. Whiteside, P. C. Hariharan, R. Seeger, and J. A. Pople, *QCPE*, 14, 368 (1979). 3-21G basis set: J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, 102, 939 (1980).

Table II. Calculated Energy Difference (kcal/mol) between Planar and 160° Boat Conformations of Dihydro Aromatics **1**-**3**[a,b]

| compd | molecular mechanics MMI | MM2 | MINDO/3 | MNDO | ab initio (3-21G)[c] |
|---|---|---|---|---|---|
| 1 | 1.2 | 0.9 | 1.9 | 0.9 | 1.2 |
| 2 | 0.8 | | | | |
| 3 | 0.4 | | 0.4 | | |

[a] For the MO calculations the planar and boat conformations had rigorous $D_{2h}$ and $C_{2v}$ symmetries, respectively. [b] The dihedral angle for the boat is defined in footnote 7. [c] All geometric parameters were completely optimized at the 3-21G level except those of the vinyl hydrogens (for which the values calculated with MINDO/3 were used as the input data).

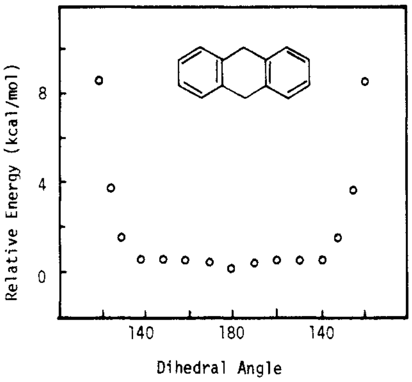


**Figure 3.** MMI energy profile of **3**.

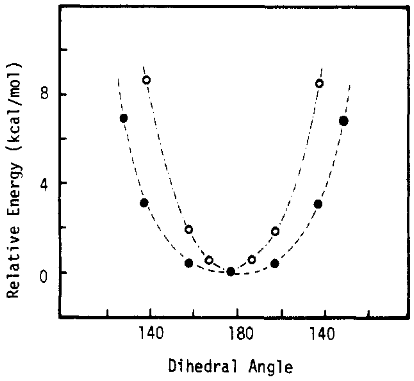


**Figure 4.** MINDO/3 energy profiles of **1** (open circles) and **3** (filled circles).

## Results and Discussion

Previous calculational studies[12-16] of 1,4-dihydrobenzene have generally indicated the planar form of **1** to be most stable. However, a detailed description of the energy surface has not been reported. We have now investigated **1**-**3** thoroughly by means of molecular mechanics[9] calculations, and the accuracy and reliability of the results have been further evaluated with semiempirical (MINDO/3 and MNDO)[10] and ab initio[16] calculations. Figures 1-3 summarize the molecular mechanics calculations by using Allinger's MMI[9a,b] force field. The results for **1** indicate an energy minimum corresponding to the planar structure **1a**, in good agreement with an earlier report by Allinger.[12] The structural parameters obtained for **1** by various methods are summarized in Table I. Somewhat surprisingly, the planar geometry is also found by MMI to be the most stable for both **2** and **3**, although the energy well is quite shallow, especially in the case of **3**.

In order to verify the reliability of the molecular mechanics results, we also studied **1** by means of MINDO/3,[10a] MNDO,[10b] and ab initio[11] calculations. Qualitatively, the results from all five methods are quite similar, although the energy well as calculated by MINDO/3 (Figure 4) is somewhat steeper than that indicated by the other calculations. The heats of formation calculated by MMI (23.9 kcal/mol) and by MM2 (26.1 kcal/mol) are in good agreement with an estimated experimental value of about 26 kcal/mol;[17] MINDO/3 and MNDO, on the other hand, give lower values of 17.8 and 14.3 kcal/mol, respectively. The energy profile for 9,10-dihydroanthracene (**3**) was also evaluated with MINDO/3 (Figure 4), and comparable results were obtained. The energy well calculated with MINDO/3 is again somewhat steeper than that obtained by using molecular mechanics, but the results of the two methods are qualitatively very similar.

Although the minimum energy structures for **1**-**3** in each case were indicated to be planar, the calculated energy wells (Figures 1-4) are quite flat. The energies required for 20° distortions from planarity for **1**-**3** (Table II) are about 1 kcal/mol or less and decrease in the order **1** > **2** > **3** due to the interplay of angle strain and torsional effects. The particularly small energy required for distortion of **3** (Figure 3) permits explanation of the otherwise contradictory experimental result[6] for this compound. The extremely flat energy surface for **3** suggests that the nonplanar X-ray structure may not represent the preferred geometry in solution or in the gas phase. The thermal energy available at room temperature ($RT = 0.6$ kcal/mol) and the entropy contributions will presumably result in large puckering amplitudes, particularly in the case of **3**, and this will influence significantly any experimental measurements made on these compounds. Such perturbation of experimental observations has already been suggested for **1**,[5a,c-f,9] and a recent study showing a temperature dependence of 1,4-proton coupling constants in partially deuterated **1** provides additional support for this conclusion.[18] While the parent compounds **1**-**3** are all found to have minimum energy structures which are planar, this may not be true for their derivatives. The actual conformations of substituted dihydro aromatic compounds may well be determined by the conformational preferences of whatever substituents are present.[19]

**Note Added in Proof.** We have also studied **3** with MM2 and MNDO calculations. Both methods afford an optimum geometry which is nonplanar (159° for MNDO),

---

(12) N. L. Allinger and J. T. Sprague, *J. Am. Chem. Soc.*, **94**, 5734 (1972).

(13) G. Ahlgren, B. Akermark, and J. E. Backvall, *Tetrahedron Lett.*, 3501 (1975). This ab initio study led to an excessively large (7.0 kcal/mol) difference between **1b** and **1a** (159.3° conformation) due to the lack of geometry optimization.

(14) S. Saebø and J. E. Boggs, *J. Mol. Struct.*, **73**, 137 (1981).

(15) (a) F. Herbstein, *J. Chem. Soc.*, 2292 (1959); (b) J. L. Marshall and L. Hall, *Tetrahedron*, **37**, 1271 (1981).

(16) A. J. Birch, A. L. Hinde, and L. Radom, *J. Am. Chem. Soc.*, **103**, 284 (1981).

(17) S. W. Benson, F. R. Cruikshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969), footnote 33; J. P. Pedley and J. Rylance, "Sussex-NPL Computer Analyzed Thermochemical Data", University of Sussex, England, 1977.

(18) M. C. Grossel and M. J. Perkins, *Nouv. J. Chim.*, **3**, 285 (1979).

(19) P. W. Rabideau and E. G. Burkholder, *J. Org. Chem.*, **44**, 2354 (1979).

although the energy surface in MM2 is too flat to determine the specific geometry. In any case, the energy difference between planar and optimum structures is less than 0.5 kcal/mol for each method, and hence our overall conclusion remains unchanged.

**Acknowledgment.** This work was supported in part by the U.S. Department of Energy, Office of Basic Energy Sciences (P.W.R.), the Indiana University Research Foundation (K.B.L.), the Alexander von Humboldt Stiftung (D.J.R.), and the Fonds der Chemischen Industrie. We thank the Indiana University Computer Network and the Regionales Rechenzentrum, Universität Erlangen-Nürnberg, for use of their facilities.

**Registry No.** 1, 628-41-1; 2, 612-17-9; 3, 613-31-0.

---

# The System Aluminum Chloride-Acetyl Chloride in Sulfur Dioxide Solvent

Boris Glavincevski and Sydney Brownstein*[1]

*Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R9*

*Received November 20, 1981*

Nuclear magnetic resonance studies of the system aluminum chloride-acetyl chloride in sulfur dioxide as solvent show the existence of complexes with two and one aluminum chloride per acetyl chloride. Equilibrium constants and exchange rates for these complexes were determined as a function of temperature and some conclusions were reached on the mechanism of the exchange reactions.

## Introduction

The system aluminum chloride-acetyl chloride is one of the fundamental reagents of the Friedel-Crafts acylation reaction and is of some industrial importance.[2] From the first report of the aluminum chloride-acetyl chloride complex[3] until the present there have been many studies of it by infrared,[4-6] nuclear magnetic resonance[7-9] and X-ray crystallography,[10] and the subject has been reviewed.[11] The consensus of opinion is that this compound exists in solution as an equilibrium mixture of ionic and molecular forms whose relative concentrations depend on solvent and temperature. In fact, for antimony pentachloride and *p*-toluoyl chloride both forms have been isolated as crystalline solids.[12] Nevertheless we will show that, at least in sulfur dioxide as solvent, a solution of acetyl chloride and aluminum chloride contains only a one 1:1 complex, in addition to a complex with two aluminum chloride entities for each acetyl chloride and free acetyl chloride and aluminum chloride.

## Experimental Section

Acetyl chloride was purified by fractional distillation. Aluminum chloride was purified by repeated vacuum sublimation. Sulfur dioxide was dried over $P_2O_5$ and stored over mercury.

**Table I.** $^{27}Al$ and $^1H$ Chemical Shifts and Line Widths for Species of Interest to the System $AlCl_3$-$CH_3COCl$ in $SO_2$ as Solvent

| sample | $\Xi(^{27}Al)$ | $\Delta^{27}Al$, Hz | $\delta\,^1H$ |
|---|---|---|---|
| $AlCl_3$ | 26 058 956 | 80 | |
| $(CH_3)_4NAlCl_4$ | 26 059 270[14] | <10 | |
| $(CH_3)_2OAlCl_3$ | 26 059 489[14] | | |
| $3AlCl_3$ + $CH_3COCl$ | 26 059 275 (strong) | | |
| | 26 059 497 (weak) | | |
| $2AlCl_3$ + $CH_3COCl$ | 26 059 256 | | 3.20 |
| | 26 059 513 | | 4.18 |
| $AlCl_3$ + $CH_3COCl$ | 26 059 276 (weak) | 120 | 3.20 |
| | | | 4.18 |
| | 26 059 535 (strong) | 15 | 2.70 |
| $AlCl_3$ + $2CH_3COCl$ | 26 059 537 | <40 | 3.20 (very weak) |
| | | | 4.18 (weak) |
| | | | 2.70 (strong) |
| $CH_3COCl$ | | | 2.70 |

Samples were prepared by quickly transferring, in a drybox, some aluminum trichloride to an NMR sample tube closed with a stopcock. Known quantities of vapor of the other two compounds were then transferred on a greaseless vacuum line onto the weighed quantity of aluminum chloride, and the sample was sealed under vacuum. All concentrations are reported as mole fractions and calculations of equilibrium and rate constants are made with this concentration unit.

Proton resonance spectra were obtained in the Fourier transform mode on a Varian Associates XL-100 spectrometer equipped with a Nicolet computer and its pulsing and power amplifier components operating at 100.1 MHz. The variable-temperature apparatus was calibrated via a methanol sample. Aluminum-27 spectra were obtained at 26.08 MHz with a Nicolet multinuclear probe and the associated mixing circuits. Proton chemical shifts are reported relative to tetramethylsilane signals as zero. Aluminum chemical shifts are reported as $\Xi$ values, with $\Xi$ for $Al(H_2O)_6^{3+}$ as 26 056 780 Hz.[13,14] Tetramethylsilane slowly reacts with aluminum trichloride, so those samples used for de-

---

[1] Issued as NRCC No. 19970.

[2] Olah, G. A., Ed. "Friedel-Crafts and Related Reactions"; Interscience: New York, 1963; Vol. 1, p 91.

[3] Boeseken, J. *Recl. Trav. Chim. Pays-Bas* **1901**, *20*, 102.

[4] Cook, D. *Can. J. Chem.* **1959**, *37*, 48.

[5] Cassimatis, D.; Bonnin, J. P.; Theophanides, T. *Can. J. Chem.* **1970**, *48*, 3860.

[6] Germain, A.; Commeyras, A.; Casadevall, A. *Bull. Soc. Chim. Fr.* **1972**, *8*, 3177.

[7] Wilinski, J.; Kurland, R. J. *J. Am. Chem. Soc.* **1978**, *100*, 2233.

[8] Olah, G. A.; Moffatt, M. E.; Kuhn, S. J.; Hardie, B. A. *J. Am. Chem. Soc.* **1964**, *86*, 2198.

[9] Haraguchi, H.; Fujiwara, S. *J. Phys. Chem.* **1969**, *73*, 3467.

[10] Le Carpentier, J. M.; Weiss, R. *Acta Crystallogr., Sect. B* **1972**, *28*, 1421.

[11] Chevrier, B.; Weiss, R. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 1.

[12] Chevrier, B.; Le Carpentier, J. M.; Weiss, R. *J. Am. Chem. Soc.* **1972**, *94*, 5718.

[13] McFarlane, W. *Ann. Rev. NMR Spectrosc.* **1968**, *1*, 135.

[14] Glavincevski, B.; Brownstein, S. *Can. J. Chem.* **1981**, *59*, 3012.

0022-3263/82/1947-1005$01.25/0