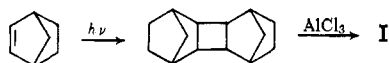


Figure 1. The mass spectrum of congressane.

zation of tetrahydrodicyclopentadiene to adamantane (II),^{4,5} by the agency of strong Lewis acid catalysts. Under such conditions, rearrangement pathways available to hydrocarbons are very favorable mechanistically, and extremely complicated transformations can be effected, often in high yields.^{5,6}

We felt that congressane (I) might be preparable by a similar rearrangement route. For a starting material, an isomeric pentacyclic alkane was needed, and such molecules have recently become available by the photodimerization of norbornene (III) in the presence of various photosensitizing agents.⁷ Samples of two stereoisomeric norbornene dimers (IV) or their mixture were heated with about one-third of their weight of AlCl_3 to increasingly higher temperatures, while monitoring the reactions by gas chromatography. Unfortunately, large quantities of tar were produced, but in addition small amounts (in these initial nonoptimum experiments, from traces to about 1%) of a high melting substance formed.



The properties of the new material were consistent with those expected of congressane and were so similar to those of adamantane (II)⁵ that we were encouraged to favor the hoped for structure, I.⁸ The melting point of congressane, 236–237°, was almost as high as that of adamantane, m.p. 268–269°. The empirical formula was $\text{C}_{14}\text{H}_{20}$ (Anal. Calcd. for $\text{C}_{14}\text{H}_{20}$: C, 89.29; H, 10.71. Found: C, 89.17; H, 10.74), and the expected molecular weight was confirmed dramatically in the mass spectrum of congressane (Figure 1). The parent peak at m/e 188 not only was the base peak, but its intensity was more than three times greater than that of any other ion. The fragmentation tendency of hydrocarbons in the mass spectrograph is very high, even for low molecular weight materials, but with congressane (as with adamantane)⁵ the interlocking system of rings ensures unusual

(4) P. von R. Schleyer and M. M. Donaldson, *J. Am. Chem. Soc.*, **82**, 4645 (1960); P. von R. Schleyer, *ibid.*, **79**, 3292 (1957).

(5) For a review, see R. C. Fort, Jr., and P. von R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

(6) A. Schneider, R. Warren, and E. J. Janoski, *J. Am. Chem. Soc.*, **86**, 5365 (1964).

(7) (a) D. Scharf and F. Korte, *Tetrahedron Letters*, 821 (1963); (b) R. D. Arnold, D. J. Trecker, and E. B. Whipple, to be published.

(8) P. von R. Schleyer and C. Cupas, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, Abstracts, p. 8U.

stability of the molecular ion. The second most intense peak in the mass spectrum, at m/e 91, is suggestive of the tropylium C_7H_7^+ ion⁹ which might be produced by splitting of the congressane molecular ion symmetrically down the middle, rearrangement, and loss of three hydrogens. The n.m.r. spectrum also was interesting, since only a single relatively sharp ($w_h \cong 3$ c.p.s.) signal at τ 8.32 was observed. The chemical shifts of the two kinds of protons of adamantane fortuitously are almost identical (τ 8.22)⁵ and the same is true for the three kinds of protons of congressane. Finally, the very simple infrared spectrum of I indicated a highly symmetrical structure. Besides the CH stretching bands (at 2908, 2878, and 2851 cm^{-1}) and CH_2 deformations (at 1442 and 1457 cm^{-1}) there was only one other absorption of more than very weak intensity (at 1047 cm^{-1}) out to 16 μ . The Raman spectrum had bands at 2926, 2907, 2880, 2851, 1444, 1308, 1233, 1179, 1086, 1072, 1039, 982, 935, and 708 cm^{-1} (CCl_4 solution).

None of these data, however, proves the congressane structure. This was done by X-ray analysis, reported separately.¹⁰

The chemistry of adamantane has now been well worked out,⁵ and congressane should behave in much the same way, with the added complication that there are now two kinds of bridgehead positions readily substitutable under ionic conditions. We will report on the chemistry of congressane subsequently, as well as on attempts to prepare congressane homologs by rearrangement.

Acknowledgments. We wish to thank the Petroleum Research Fund, administered by the American Chemical Society, for support of this research at Princeton University. We appreciate especially the efforts of Drs. I. L. Karle and J. Karle, who determined the X-ray structure of congressane.¹⁰

(9) See S. Meyerson, J. D. McCollum, and P. N. Rylander, *J. Am. Chem. Soc.*, **83**, 1401 (1961); F. Meyer and A. G. Harrison, *ibid.*, **84**, 4757 (1964).

(10) I. L. Karle and J. Karle, *ibid.*, **87**, 918 (1965).

(11) Alfred P. Sloan Foundation Fellow, 1962–1966; Fulbright Research Fellow and J. S. Guggenheim Fellow at the Institute of Organic Chemistry of the University of Munich, Munich, Germany, 1964–1965

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The Crystal and Molecular Structure of Congressane, $\text{C}_{14}\text{H}_{20}$, by X-Ray Diffraction

Sir:

A structure analysis by X-ray diffraction of the material described in the accompanying communication by Cupas, Schleyer, and Trecker¹ has verified that the material is congressane (I).

A fragment of a large octahedron grown from petroleum ether was mounted on the a axis and was used to take eight layers of equi-inclination Weissenberg photographs with $\text{Cu K}\alpha$ radiation. Visual estimates were

(1) C. Cupas, P. von R. Schleyer, and D. J. Trecker, *J. Am. Chem. Soc.*, **87**, 917 (1965).

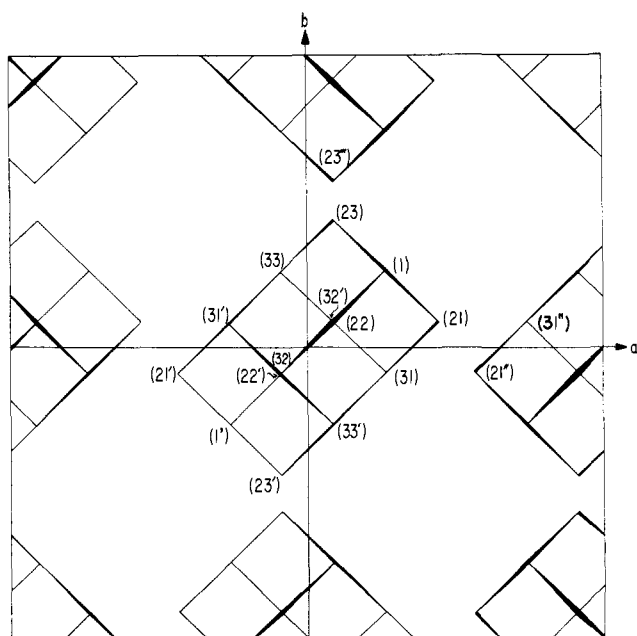


Figure 1. Contents of the unit cell of congressane projected along the (001).

made of the intensities. The material crystallizes in the cubic system, space group Pa3, $a = 10.109 \pm 0.02$ Å, $Z = 4$, and $\rho_{\text{X-ray}} = 1.210$ g./cm.³.

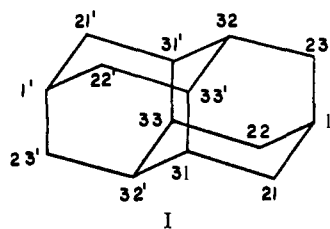


Table I

	x	y	z
C(1)	0.1333	0.1333	0.1333
C(21)	0.2193	0.0456	0.0434
C(31)	0.1312	-0.0421	-0.0438
H(1)	0.1907	0.1907	0.1907
H(2,1)	0.2587	0.0973	-0.0320
H(2,2)	0.2523	-0.0120	0.0911
H(3)	0.1824	-0.1085	-0.0920

Table II

Bond	Å.	Angle	Degrees
C(1)-C(21)	1.538 ± 0.005	C(21)-C(1)-C(22)	108° 45' ± 25'
C(21)-C(31)	1.535 ± 0.005	C(1)-C(21)-C(31)	110° 10' ± 25'
C(31)-C(32')	1.532 ± 0.005	C(21)-C(31)-C(32')	110° 10' ± 25'
		C(31)-C(32')-C(33)	108° 43' ± 25'
C(1)-H(1)	1.00 ± 0.10		
C(21)-H(2,1)	1.01 ± 0.10		
C(21)-H(2,2)	0.83 ± 0.10		
C(31)-H(3)	0.98 ± 0.10		

The molecule of congressane occurs in the unit cell with its center of symmetry on the origin and atoms (1) and (1') along the body diagonal. Carbon atom (1)

and its equivalents occupy the 8-fold positions (c); and carbon atoms (2) and (3) with their equivalents occupy the 24-fold positions (d) as described in the "International Tables for X-Ray Crystallography."² The placement of the four molecules in the unit cell is illustrated in Figure 1. Of the four crystallographically independent hydrogen atoms, H(1) attached to C(1) lies on the body diagonal of the cell; and H(2,1) and H(2,2) attached to C(21), and H(3) attached to C(31), each occupy 24-fold positions (d). The coordinates expressed as fractions of the unit cell are shown in Table I.

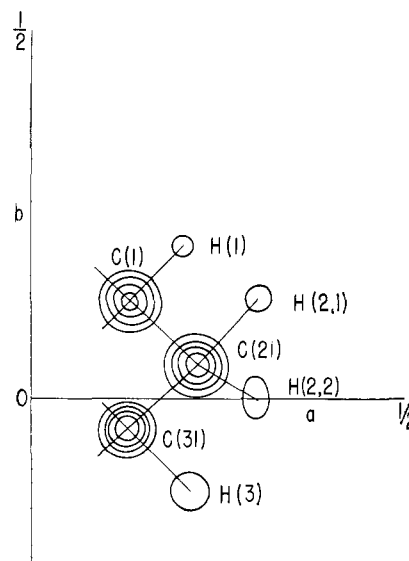


Figure 2. Sections of a three-dimensional E-map projected along the (001). E-maps are Fourier's computed with normalized structure factor E values for coefficients rather than F values.

This highly symmetric structure was solved by inspection since the congressane molecule has a threefold rotation axis connecting atoms (1) and (1'), and space group Pa3 has a threefold rotation axis along the body diagonal. The structure was confirmed by determining phases directly from the intensities by the symbolic addition procedure³ and computing an E-map with the 71 largest $|E|$ magnitudes which is illustrated in Figure 2. The E-map clearly indicates both the carbon and hydrogen atoms in the asymmetric unit. A least-squares refinement on the coordinates

and the temperature factors of the carbon and hydrogen

(2) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p. 314.

(3) I. L. Karle and J. Karle, *Acta Cryst.*, **16**, 969 (1963).

atoms resulted in an R factor of 11% for 325 independent data.

The interatomic distances and angles are shown in Table II. Nearest approaches between molecules are $C(1) \cdots C(31'')$ at 4.14 Å. and $C(1) \cdots C(23'')$ at 4.52 Å.

It is seen that all the bonded C–C distances are near 1.54 Å., the diamond value, and all the angles are near the tetrahedral value. Adamantane,⁴ the single cage structure related to congressane, also crystallizes in the cubic system and has C–C bond distances of 1.54 Å. and tetrahedral bond angles. It is of interest that the nearest approach between molecules of adamantane is the same as that for congressane. Both substances have unusually high densities for hydrocarbons, namely, 1.07 g./cm.³ for adamantane and 1.21 g./cm.³ for congressane.

Acknowledgment. We wish to thank Dr. P. Schleyer for suggesting that we investigate the structure of congressane, Dr. Schleyer and Mr. C. Cupas for furnishing us with the crystal, and Mr. S. Brenner for performing the calculations.

(4) W. Nowacki, *Helv. Chim. Acta*, **28**, 1233 (1945).

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The Inductive Effect in the Toluene Anion Radical

Sir:

The general agreement found between the aromatic ion-radical spin densities calculated by molecular orbital theory and estimated from electron spin resonance hyperfine splittings is considered an important experimental confirmation of π -electron theory.¹ A prime example of this type of comparison is provided by the toluene anion.² For this radical a simple, yet relatively accurate, description of the measured ring hyperfine splittings is obtained by assuming that the double degeneracy of the benzene anion ground state is lifted by the presence of the methyl group and that the unpaired electron is in the lower energy orbital, which is the one that is "antisymmetric" with respect to the perpendicular plane through the substituted carbon (C_1) and the *para* carbon (C_4). This orbital (often designated as Ψ_5) has the form

$$\Psi_5 = \frac{1}{\sqrt{4}}(\phi_2 - \phi_3 + \phi_5 - \phi_6) \quad (1)$$

where the ϕ_i are atomic π -orbitals associated with carbon C_i . Equation 1 yields spin densities of $1/4$ in the 2-, 3-, 5-, and 6-positions and zero in the 1- and 4-positions in correspondence with the e.s.r. result that there are four large hyperfine constants of nearly equal magnitude ($|a^H| \cong 5.3$ gauss) due to the 2-, 3-, 5-, and 6-ring protons and very small splitting constants from the ring proton in the 4-position and from the methyl group protons. Although this interpretation is almost certainly correct, we wish to point out that it is not consistent with a calculation based on the most common model for the methyl group

(1) See, for example, A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 6.

(2) J. R. Bolton and A. Carrington, *Mol. Phys.*, **4**, 497 (1961).

ring interaction; that is, if a Hückel molecular orbital (HMO) treatment with the Mulliken hyperconjugative model³ and Coulson–Crawford parameters⁴ for the methyl group is performed, it is found that the *symmetric* member of the degenerate benzene orbitals has a lower energy. Since this orbital (Ψ_4) has the form

$$\Psi_4 = \frac{1}{\sqrt{12}}(2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6) \quad (2)$$

it yields two large spin densities ($1/3$) in the 1- and 4-positions and four small ones ($1/12$) in the 2-, 3-, 5-, and 6-positions. Thus, the result that Ψ_4 is more stable in the toluene anion and, therefore, is occupied by the unpaired electron is clearly in disagreement with the e.s.r. spectrum.

The difficulty with the Coulson–Crawford model can be described in a simple manner. Since the antisymmetric orbital (Ψ_5) has no contribution from the atomic orbital ϕ_1 at the methyl-substituted position, it has exactly the HMO energy that it would have in the benzene anion. Only the energy of the symmetric orbital (Ψ_4) is altered by the substitution and a *stabilization* is produced by conjugation with the methyl group. To consider this effect in more detail, we number the significant positions C_1 , C_7 , and X_8 , where C_1 is the benzene carbon, C_7 is the methyl group carbon, and X_8 is the hydrogen group pseudo-atom. The essential parameters for the interacting methyl group are

$$\begin{aligned} \alpha_7 &= \alpha_0 + h_7\beta_0 & \beta_{17} &= k_{17}\beta_0 \\ \alpha_8 &= \alpha_0 + h_8\beta_0 & \beta_{78} &= k_{78}\beta_0 \end{aligned}$$

where α_0 and β_0 are the ring-carbon atomic integral and resonance integral, respectively; and h_7 , h_8 , k_{17} , and k_{78} are proportionality constants selected by some fitting procedure.^{1,4} With the Coulson–Crawford values $h_7 = -0.1$, $h_8 = -0.5$, $k_{17} = 0.7$, and $k_{78} = 2.5$, one finds for the symmetric orbital energy $\epsilon_4 = \alpha_0 - 0.986\beta_0$, while the antisymmetric orbital has the unperturbed energy $\epsilon_5 = \alpha_0 - \beta_0$. Variation of the methyl group parameters, (h_7 , h_8 ; k_{17} , k_{78}) within reasonable ranges does not alter the order of the energy levels. Independent of k_{17} and k_{18} , α_8 has to be increased to $\alpha_0 - 1.0\beta_0$ to make ϵ_4 and ϵ_5 degenerate, while a still larger value of α_8 is needed to make the energy level differences ($\epsilon_4 - \epsilon_5$) have the required positive sign.

The paradox that emerges from the above calculation can be solved by introducing an additional parameter corresponding to the inductive effect⁵ of the methyl group on the ring carbon atoms, in particular on the substituted position C_1 . Writing $\alpha_1 = \alpha_0 + h_1\beta_0$, and using the previously listed values for the methyl group, one finds that $\epsilon_4 - \epsilon_5 \cong (1/3)h_1\beta_0$. Thus, a "chemically" reasonable negative h_1 can produce the correct ordering of the energy levels; a value on the order of -0.1 seems to be needed to produce the proper energy level splitting. Such a value for h_1 is not out of line with estimates based on other molecular properties. What is important about the e.s.r. data is that their "all or nothing" character seems to

(3) R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941).

(4) C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, 2052 (1953).

(5) See ref. 1, Section 5.7. The simple inductive model [G. W. Wheland and L. Pauling, *J. Am. Chem. Soc.*, **57**, 2086 (1935)] yields the correct order for the energy levels but no methyl group hyperfine splittings.