tion of the AO used by carbon to form a C–X σ bond should have more p character, the more electronegative X, and that this should lead to a corresponding decrease in the bond angles Y–C–X involving X. He quoted a number of examples in support of this concept which have recently been used extensively by Pauling[12] to explain the pyramidal structure of radicals such as $\cdot CF_3$. However, the electronegativity effect cannot explain the apparent nonplanarity of *tert*-butyl nor the fact[7] that $\cdot C(CF_3)_3$ is more planar, not less planar, than $\cdot C(CH_3)_3$. We would have predicted this since the binding energy of the C–C bond electrons must be greater in $\cdot C(CF_3)_3$. Another example is the apparent failure of the highly electronegative quaternary ammonium to induce nonplanarity at an adjacent radical center.[13] Our analysis also accounts for this, since the binding energy of the electrons in the C–N$^+$ bond must be very great. We would also have predicted that the barrier to inversion in 1-trifluoromethylcyclopropyl radicals would be much lower than in 1-fluorocyclopropyl ones, as is in fact the case.[14]

As a further check we have carried out MINDO/3[15] calculations for the substituted vinyl and cyclopropyl radicals **1** and **2** and for the corresponding linear and planar conformations; tests indicated that the true transition states for inversion differ negligibly from these in energy. All the geometries were calculated by complete minimization of the energy with respect to all geometrical variables. The corresponding barriers to inversion are shown in Table I.

Table I. Calculated Inversion Barriers (E_a) of Vinyl and Cyclopropyl Radicals Calculated by MINDO/3

	E_a, kcal/mol			E_a, kcal/mol	
Substrate	Cis → trans	Trans → cis	Substrate	Cis → trans	Trans → cis
1a	8.5	8.5	**1g**	7.5	8.5
1b	6.2	6.2	**2a**	4.6	4.6
1d	5.0	2.6	**2b**	5.9	5.9
1e	9.7	9.8	**2d**	2.8	3.4
1f	7.1	8.2	**2e**	4.8	4.7

The orbitals interacting with the radical center are the C–X σ bond MO and a lone-pair AO of R.[17] The binding energies of the C–X bond electrons increase in the order C–C < C–H < C–Cl. Likewise those of lone-pair electrons increase in the order O < Cl < F. Our arguments therefore imply that for a given group X in **1** or **2**, the barrier to inversion should increase in the order (R=) O < Cl < F. Our results follow this pattern: *e.g.*, **1b** < **1a** and **2a** < **2b**. Likewise, for a given group R, the barriers should increase in the order (X=) Cl < H < C. Our results again agree: *e.g.*, **1d** < **1e** < **1a** and **2d** < **2a** < **2e**. Note that in the latter case the order is opposite to that predicted[11,12] on the basis of electronegativity.

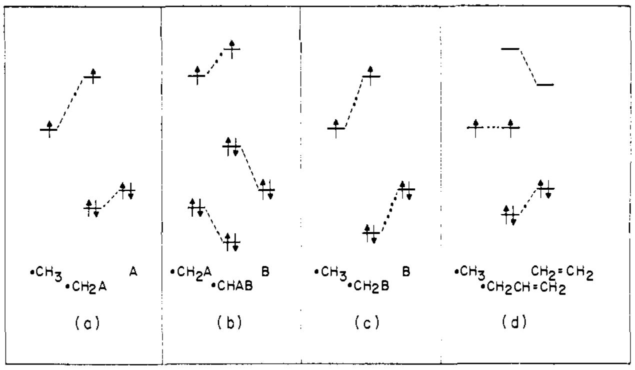

Figure 1. Interactions between (a) the singly occupied orbital of $\cdot CH_3$ and the doubly filled one of A or union to $\cdot CH_3A$; (b) the resulting MO's of $\cdot CH_2A$ and the doubly occupied orbital of B or union to $\cdot$CHAB; (c) the singly occupied orbital of $\cdot CH_3$ and the doubly occupied one of B or union to $\cdot$CHAB.

These conclusions might at first sight seem to require radicals with two or more substituents with lone pairs at the radical center to be less stable than those with one. This of course is not the case. Thus, the C–H bond strength in $CHCl_3$ is certainly less than that in CH_3Cl. This, however, can also be easily understood in terms of our PMO approach.[18] The formation of a three-center bond by interaction of a lone pair of A with the singly occupied AO of C in $\cdot CH_2A$ is essentially[18] a first-order perturbation; it therefore varies as the first power of the C–A resonance integral. The antibonding $\cdot$CHA–B interaction is, however, a second-order perturbation and so varies as the square of the C–B resonance integral. When such a radical becomes nonplanar, the stabilizing first-order effects decrease as the first power of the resonance integral while the destabilizing second-order ones decrease as its square. Thus, additional substituents may lead to overall stabilization even though they destroy the symmetry of the radical center. The effects of such additional substituents should, however, be nonadditive, as indeed seems to be the case. Thus, while bromine atoms react much faster with methyl chloride than with methane[19a] the corresponding ratio for attack on the CH_2Cl and CH_3 groups of *n*-butyl chloride is significantly less.[19b] Likewise, the R–H bond strength decreases nonlinearly in the series Me > Et > *i*-Pr > *t*-Bu.[20]

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[12] L. Pauling, *J. Chem. Phys.*, **51**, 2767 (1968). See also ref 11.

[13] N. H. Anderson and R. O. C. Norman, *J. Chem. Soc. B*, 993 (1971).

[14] L. T. Altman and J. C. Vederas, *Chem. Commun.*, 895 (1969).

[15] MINDO/3 is a new and improved version of the MINDO[16] semiempirical SCF-MO method: R. C. Bingham, M. J. S. Dewar, and and D. H. Lo, to be submitted for publication.

[16] N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262, 1275 (1969); M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970).

[17] The other C–H bonds also interact but these contributions are the same in all cases and so do not interfere with the comparisons made here.

[18] M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

[19] See W. Thaler in "Methods in Free-Radical Chemistry," E. S. Huyser, Ed., Marcel Dekker, New York, N. Y., 1969: (a) p 150; (b) p 181.

[20] For an alternative explanation see C. Ruchardt, *Angew. Chem.*, 82, 845 (1970).

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Structure of a Novel Dimer Formed by Coupling Metal Macrocycles

Sir:

In the course of our studies of metal β-diketonates and their use in template condensation reactions for the

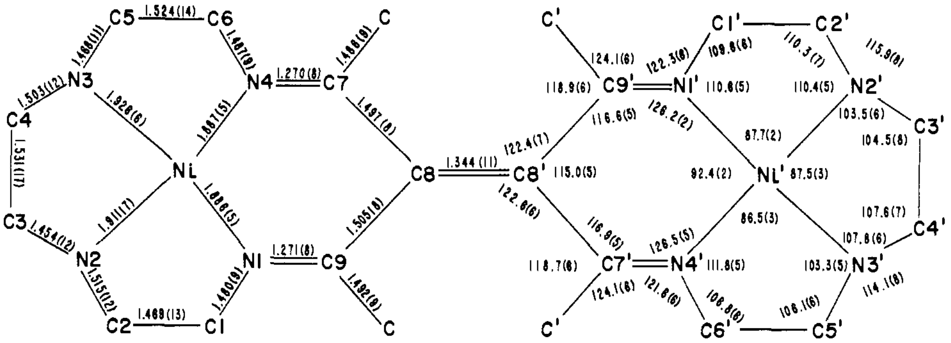

Figure 1. A schematic representation of a dimeric unit where primed and unprimed atoms are related by the crystallographic center of symmetry midway along the C8–C8′ double bond. The coordinated iodide atoms (Ni–I distance 2.961 (1) Å), one above and one below the plane of the molecule, have been omitted for clarity as well as the water molecules hydrogen bonded to N2 and N2′ at a distance of 2.907 (12) Å. The methyl–methyl contact distance is only 3.303 (12) Å.

syntheses of macrocycles, we have synthesized and determined the structure of an interesting dimer formed by the coupling of two macrocyclic rings *via* a carbon–carbon double bond. In earlier work the diamagnetic, 13-membered macrocyclic complex 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienatonickel(II) (hereafter abbreviated [NiAT]$^-$) was synthesized[1,2] and the structure[3] of the orange perchlorate salt was determined. Elfring and Rose[4] showed that protonation of this complex at the methine carbon is readily achieved at pH ~3 and the resulting complex can be isolated as a diamagnetic, yellow-orange product with a variety of anions. A shift of +135 cm^{-1} in the infrared spectrum was reported for the C═N stretch. In the present study an aqueous solution of [NiAT]I was chilled to 5° and the pH was adjusted to and maintained at ~1 by the addition of acetic acid. In 2–3 weeks black crystals were obtained. With respect to both the protonated and nonprotonated monomers several differences in the infrared spectra of the dimer were noted. Relative to [NiAT]I, the C═N and/or C═C stretching frequencies have been increased by 75 cm^{-1}. Absorption bands in the visible spectrum appear at 356 and 315 mμ, no band is observed in the 485-mμ region. For the parent monomer the band observed at 485 mμ was assigned to a transition consistent with the presence of square-planar nickel(II). No absorptions in the proton nmr were observed for 5% solutions (by weight) of the dimer in either D_2O or CD_3CN despite the diamagnetic nature of the solid. The use of less polar and presumably noncoordinating solvents was prevented by limited solubilities. Because of the unusual nature of the macrocycle dimer and its significance both as a model for the biologically important compounds as well as suggesting a new route for the syntheses of coordination polymers, we have determined the crystal and molecular structure and report it herein.

A single crystal with dimensions 0.49 × 0.28 × 0.12 mm was mounted on the end of a thin glass fiber. Precession photographs clearly showed the Laué symmetry $2/m$ and displayed systematic extinctions suggesting $P2_1/n$ as the uniquely probable space group.[5] The goniometer head and crystal were transferred to an automated Picker four-circle diffractometer equipped with a molybdenum target X-ray tube and a graphite monochromator ($\lambda_{K\alpha_1}$ 0.70926 Å). Ambient laboratory temperature was 20 ± 1°. Precision lattice constants of $a = 13.082$ (4), $b = 15.902$ (6), $c = 8.453$ (5) Å, and $\cos \beta = -0.1452$ (5) giving $\beta = 98° 21'$ were calculated from a least-squares treatment of the setting angles for 48 reflections.[6] These lattice constants together with a measured density of 1.95 (1) g cm^{-3} indicate the unit cell contains two dimeric units ($\rho_c = 1.96$ g cm^{-3}).

The intensities of all independent reflections in the range $0.030 \leq (\sin \theta)/\lambda \leq 0.743$ were measured by the θ–2θ scan technique; background was measured for 20 sec at the limits of the scan. The width of the scan, traversed at the rate of 1°/min, consisted of a 1.6° range for estimated base width at $2\theta = 0°$ plus a variable increment to account for spectral dispersion. After correction for background, the intensities of the 5986 independent reflections were reduced to a set of relative scattering amplitudes, $|F_o|$, by the application of Lorentz, polarization, and absorption corrections.[7] The 4808 reflections satisfying the criterion $|F_o| \geq 3\sigma|F_o|$ were used to develop and refine the structure by the usual heavy-atom methods, wherein $\sigma|F_o|$ is obtained from a consideration of only counting statistics. Initial trial positions for the nickel and two iodine atoms were deduced from a three-dimensional Patterson synthesis,[8] and the positions of the remaining carbon and heavier atoms were determined from difference syntheses phased by the heavy-atom contributions. Refinement[9] of the atomic coordinates and anisotropic thermal parameters utilized a block diagonal least-squares minimization of the function, $\Sigma w(|F_o| - k \cdot |F_c|)^2$, with empirical weights ($w = \sigma^{-2}$) calculated from

$$\sigma = \sum_0^3 a_n|F_o|^n$$

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(1) S. C. Cummings and R. E. Sievers, *J. Amer. Chem. Soc.*, **92**, 215 (1970).

(2) S. C. Cummings and R. E. Sievers, *Inorg. Chem.*, **9**, 1131 (1970).

(3) M. F. Richardson and R. E. Sievers, *J. Amer. Chem. Soc.*, **94**, 4134 (1972).

(4) W. H. Elfring, Jr., and N. J. Rose, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 14–18, 1970.

(5) Space group $P2_1/n$ is a nonstandard setting of $P2_1/c$: "International Tables for X-ray Crystallography, Vol. I. Symmetry Groups," The Kynoch Press, Birmingham, England, 1965, p 99.

(6) Use was made of the PICK II computer program, a revision in this laboratory of W. C. Hamilton's Mode I program.

(7) D. J. Wehe, W. R. Busing, and H. A. Levy, "ORABS, A Fortran Program for Calculating Single Crystal Absorption Corrections," USAEC Report, ORNL-TM-229, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(8) Programs used were local version of Zalkin's fourier program, FORDAP, and J. J. Park's block diagonal least-squares program REFINE.

(9) Atomic form factors were from D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968), with corrections, real and imaginary, for anomalous dispersion in the nickel and iodine form factors from D. T. Cromer, *ibid.*, **18**, 17 (1965).

the a_n being coefficients from the least-squares fitting of the curve

$$||F_o| - |F_c|| = \sum_0^3 a_n|F_o|^n$$

The values of $|F_c|$ were from a sensible final description of the structure; a conventional R of 0.0819 was obtained. Further refinements which include the contributions of the hydrogen atoms to the scattering are being conducted.

The most striking and unique feature of the structure is the presence of an unexpected and previously unreported dimer. A complete dimeric unit is schematically shown in Figure 1.[10] This dimer formed by linking the monomeric macrocycles through the methine carbons atoms (C8, C8′) is crystallographically required to possess a center of symmetry midway along the C8-C8′ bond. The methine carbon atoms of the monomers have been oxidatively dehydrogenated and coupled *via* a localized double bond. In an apparent effort to minimize steric crowding between the methyl groups, C8 and C8′ have each been displaced by 0.55 Å from the nearly planar arrays formed by N1, C9, C7, N4 and N1′, C9′, C7′, N4′. These displacements effectively prevent delocalization of the π electron system. The C9—N1 and C7—N4 bond distances (see Figure 1) are within the range expected for a localized C=N bond. The bonding parameters displayed in the remaining portion of the complex clearly indicate little, if any, delocalization extending into the ethylene backbones. Local coplanarity is preserved within each grouping N1, C1, C9, Ni, and N4, C6, C7, Ni; the mean deviation from exact planarity does not exceed 0.04 Å in either case. The six atom array C9, C8, C7, C7′, C8′, C9′ is virtually planar with a mean deviation from planarity of only 0.006 Å.

The four nitrogen atoms bonded to the nickel ion show departures from planarity of ±0.04 Å, and form the base of a distorted tetragonal pyramid. The nickel atom is displaced 0.30 Å from this plane toward the apical iodine atom. The remaining two iodide ions are well separated from the nickel atoms and are clearly not coordinated.

We are presently studying the applicability of this novel coupling reaction to other macrocyclic complexes. It has not escaped our notice that this coupling may offer an approach to the synthesis of coordination polymers if suitable multifunctional macrocycles are used as starting materials.

Acknowledgment. We wish to thank Dr. S. C. Cummings for making the solid-state magnetic measurement.

(10) The number in parentheses is the estimated standard deviation in the last significant figure.

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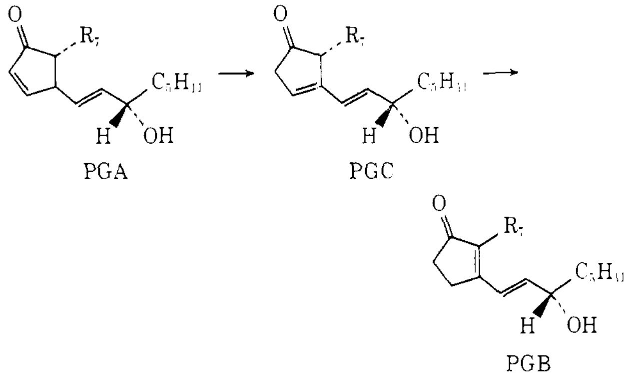
Synthetic Entry into the Prostaglandin C Series

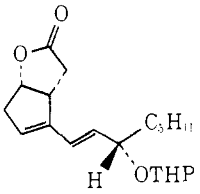
Sir:

As a result of recent work, it is now apparent that the hypertensively active A prostaglandins (PGA's) are deactivated in mammalian blood by conversion to B prostaglandins (PGB's) through the influence of an isomerase which catalyzes the conversion of PGA to a previously unstudied type of prostaglandin termed PGC.[1] The members of the PGC series are of considerable interest for a number of reasons including the fact that they appear to have substantially greater depressor activity than the PGA's.[1b] This communication reports a novel and effective method for extending the previously developed general route[2] to prostaglandins to the PGC series.



PGA PGC PGB

The lactol **1**,[2] available by a highly stereoselective and efficient synthetic route, can be transformed into PGA_2[2] and thence into various primary prostaglandins.[3] Reaction of **1** with 2 equiv of triiron dodecacarbonyl in dimethoxyethane at 95° for 30 min affords the stable, conjugated diene complex **2** as a yellow oil in 40–60% yield (not optimized). The infrared spectrum ($CHCl_3$ solution) of a sample of **2** which had been purified by thin-layer chromatography (tlc) exhibited hydroxyl absorption (3595 cm^{-1}), carbonyl absorption characteristic of diene–$Fe(CO)_3$ complexes (2040 and 1930–1950 cm^{-1}), and bands due to a tetrahydropyranyl group (1025–1070 and 1120–1170 cm^{-1}). The mass spectrum of pure **2** showed the expected molecular ion at m/e 476, and the ultraviolet spectrum showed a maximum at 227 nm (ϵ 20,000). The reaction of **2** with excess Collins reagent[4] in methylene chloride at −23° (Dry Ice-CCl_4 bath) for 30 min followed by stirring with powdered sodium bisulfate monohydrate at −23°, filtration, and evaporation produced the lactone **3** in 86% yield as a colorless oil: infrared max at 1770 cm^{-1} ($CHCl_3$ solution) due to lactone, molecular ion at m/e 334, and ultraviolet max (CH_3OH solution) at 234 nm with shoulders at 228 and 242 nm as is characteristic[1] of the PGC system. From all these data structure **2** follows unambiguously for the iron complex derived from **1**.



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(1) (a) R. L. Jones, *J. Lipid Res.*, **13**, 511 (1972); (b) R. L. Jones and S. Cammock, *Advan. Biosci.*, **9**, 61 (1973).

(2) See, E. J. Corey and G. Moinet, *J. Amer. Chem. Soc.*, **95**, 6831 (1973).

(3) E. J. Corey and H. E. Ensley, *J. Org. Chem.*, **38**, 3187 (1973).

(4) J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968).