**Table I.** Yields of $^{11}C$-Labeled Products from Reactions of $^{11}C$ and Benzene[a]

| | Gas phase — Yields as % total $^{11}C$ atoms | | | Condensed phase — Relative yields[c] | |
|---|---|---|---|---|---|
| Product[b] | Benzene, 7 cm | Benzene, 6.65 cm oxygen, 0.35 cm | Benzene, 4.0 cm neon, 76 cm | Benzene, liquid (25°) | Benzene, solid (−195°) |
| Carbon monoxide<br>Methane | 4.0 ± 0.2 | 11.0 ± 1.2[d] | 2.0 ± 1.3 | 0.9 ± 0.1 | 0.7 ± 0.1 |
| Acetylene | 7.4 ± 0.2 | 6.7 ± 0.9 | 1.9 ± 0.4 | 18.4 ± 1.6 | 14.8 ± 1.4 |
| Vinylacetylene | 0.2 ± 0.1 | 0.3 ± 0.1 | 0.2 ± 0.1 | 2.5 ± 0.4 | 3.7 ± 1.6 |
| Diacetylene | 5.3 ± 0.5 | 6.1 ± 0.6 | 1.7 ± 0.1 | 7.6 ± 0.1 | 2.7 ± 0.3 |
| Benzene | 2.3 ± 0.2 | 2.6 ± 0.4 | 0.4 ± 1.0 | 6.4 ± 0.8[e] | 12.3 ± 0.9 |
| Toluene | 0.5 ± 0.1 | 0.5 ± 0.1 | 0.3 ± 0.1 | 7.3 ± 0.9[e] | 7.7 ± 0.9 |
| Tropylidene | <0.1 | <0.1 | 0.6 ± 0.2 | 8.4 ± 2.1 | 16.8 ± 3.3 |
| Polymer | 80 ± 7 | 73 ± 5 | 93 ± 2 | | |

[a] Errors indicate the standard deviation obtained from several measurements. [b] Other volatile products found in very small yields (<0.4% absolute) in gas-phase studies were ethane, ethylene, allene, methylacetylene, 1,3-butadiene, and some unidentified $C_7$ compounds. Two other volatile products having a total volatile yield of 2.9 and 3.7% in the liquid and solid phases, respectively, are as yet unidentified, but have boiling points and bonding properties very similar to that of benzene. [c] Expressed as per cent total volatile $^{11}C$ labeled yield. Absolute yields were not determined in condensed phase. However, both Wolf[6] and Voigt[4] give 2.3% as the absolute toluene yield in the liquid phase. [d] Includes 1.6% $^{11}C$-labeled carbon dioxide. [e] Addition of 0.003% diphenylpicrylhydrazyl(DPPH) as scavenger caused no significant change in yield.

Results are shown in Table I. Benzene:toluene:tropylidene yield ratios are in reasonable agreement with those of Wolf and co-workers,[3a,6] with the exception of the reported benzene:toluene ratio in unscavenged benzene,[3a] and also agree with the most recent values of Voigt, *et al.*[4] Two $C_4$ products not previously identified, vinylacetylene and diacetylene, were found in relatively high yields.

The new gas-phase data provide the most striking features. Absolute yields of volatile ($C_1$–$C_7$) products are always low, and polymeric material is correspondingly dominant. When the carbon atoms are thermalized by neon, this tendency is even more pronounced, with the lighter products almost disappearing altogether.

A primary conclusion is that atomic carbon is extremely reactive with benzene. This is indicated by an increase in the absolute yield of carbon monoxide of only about 5% when 5 mole % oxygen is added. The reactivity of benzene is, therefore, comparable to that of oxygen, which, in turn, is similar to that of the alkenes. (See Table II of ref 9.) It is not surprising that atomic carbon adds readily to benzene. Several stable adducts with π-bonded configurations, including that of the "open-sandwich" type, can be readily conceived, and others resulting from carbon atom insertion into the C–H bonds are also possible (see Figure 1).

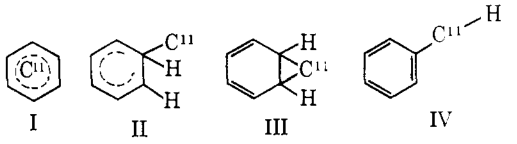

Figure 1. Some possible configuration of $^{11}C$–$C_6H_6$ adducts: (I) π-bond complex; (II, III) double bond additions; (IV) C–H bond insertion.

Adducts formed by carbon atoms with alkenes, such as ethylene[9] and cyclopentadiene,[10] frequently fragment to form stable compounds, but this appears to be more difficult in the benzene case. Such processes are energetically possible, even for benzene adducts formed by thermal carbon atoms, *e.g.*[11]

$$^{11}C + C_6H_6 \longrightarrow$$

$$C_6H_6{-}^{11}C \longrightarrow H^{11}CCH + H_2CCCHCCH \qquad \Delta H = -34\ \text{kcal}$$

$$\longrightarrow H^{11}CCCH + HCCCH_3 \qquad \Delta H = -36\ \text{kcal}$$

However, analogous reactions with alkenes are not only considerably more exoergic but, more important, require much less extensive internal rearrangement. Thus, the probability of fragmentation of the $C_6H_6$–$^{11}C$ adduct is unusually low even when a hot carbon atom provides extra driving energy. When the carbon atom has been thermalized, such processes become almost negligible. Since there is no stable $C_7H_6$ molecule to which the adducts may easily rearrange, they must eventually undergo bimolecular reaction. In view of their nature, addition of the intermediates to benzene to form polymer should readily occur. This propensity for forming polymers had previously been noted in aromatic systems[2a,12] and is obvious in the results of this work.

**Acknowledgment.** This work was carried out with the support of the Atomic Energy Commission and the help of the staffs of the Yale heavy ion and linear electron accelerators. Timothy Rose gratefully acknowledges a National Institute of Health predoctoral fellowship.

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(13) Department of Chemistry, Haverford College, Haverford, Pa.

**Timothy Rose, Colin MacKay,[13] Richard Wolfgang**
*Departments of Chemistry*
*Yale University, New Haven, Connecticut*
*Haverford College, Haverford, Pennsylvania*

*Received September 15, 1966*

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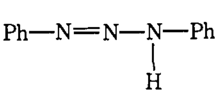
## An Octahedral Complex Containing Three Four-Membered Chelate Rings

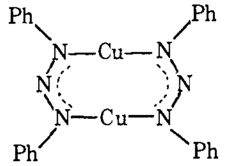
*Sir:*

1,3-Diphenyltriazene (I) (commonly referred to as diazoaminobenzene and abbreviated as Hdpt) forms a series of metal derivatives which have a structural form very closely related to that observed for copper(II) acetate monohydrate.[1,2] For example, the crystal structure determination of the copper(I) compound, Cu(dpt), has shown that it possesses a binuclear structure (II).[1] The simple derivatives of copper(II), nickel(II), and palladium(II) are also binuclear and this together with the observed diamagnetism of the copper(II) compound suggests that the structures of these three compounds closely parallel that of copper(II) acetate monohydrate.[2]



$\mathrm{Ph{-}N{=}N{-}\underset{\displaystyle H}{\underset{|}{N}}{-}Ph}$

I



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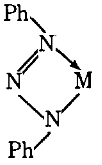
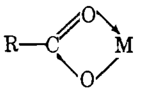


III

The structures originally formulated for the metal derivatives of both 1,3-diphenyltriazene[3] and the carboxylic acids[4] involved four-membered chelate rings (III and IV). These formulations were criticized on the grounds there would be considerable steric strain and distortion of the natural valency angles.[2,5] The molecular geometry observed or now proposed for these compounds is based on a system (V and VI) such that the steric strain associated with four-membered chelate rings is eliminated.



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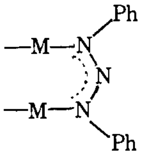
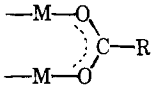


V



VI

Recently, the cobalt(III) derivative of 1,3-diphenyltriazene, Co(dpt)$_3$, has been prepared by Dubicki and Martin.[6] We have determined the crystal structure of this compound and have found surprisingly that the cobalt atom is surrounded by three ligand groups, each with two nitrogen atoms bonded at normal covalent distances to the metal atom. The ligand groups therefore function as bidentates so that a four-membered chelate ring structure is assumed. The crystal data are for tris(1,3-diphenyltriazenido)cobalt(III)-toluene ($C_{43}H_{38}N_9Co$), mol wt, 739.8: monoclinic, $a$ = 20.84, $b$ = 16.27, $c$ = 13.41 A; $\beta$ = 120.5°; $D_m$ = 1.26, $Z$ = 4, $D_c$ = 1.25 g cm$^{-3}$; space group C2/c ($C_{2h}^6$, No. 15); Co(unfiltered) radiation, single crystal oscillation, and equi-inclination Weissenberg photographs.

The coordinates of the cobalt atom were obtained from a three-dimensional Patterson function; the cobalt atom occupies a position with site symmetry 2. The carbon and nitrogen atoms were located in subsequent three-dimensional electron density distributions and the structure is being refined by the method of least squares. At present, the $R$ value is 0.15 based on the observed reflections only and using individual isotropic temperature factors.

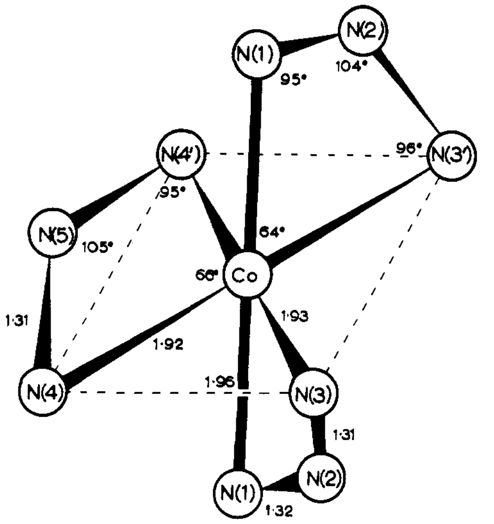


Figure 1. The metal environment of the cobalt(III) derivative of 1,3-diphenyltriazene.

The crystals of the compound are molecular consisting of discrete units of composition Co(dpt)$_3$, together with one toluene molecule per Co(dpt)$_3$ unit which is present in the lattice as solvent of crystallization. Passing through both these molecules is a twofold crystallographic axis and each molecular unit is separated from all its neighbors at the normal van der Waals distances. Each cobalt atom is situated in a distorted octahedral environment; the two apical nitrogen atoms are displaced considerably from the perpendicular to the plane containing the other four cobalt-bound nitrogen atoms. This is shown in Figure 1 which gives the molecular geometry of Co(dpt)$_3$ units together with some of the important dimensions.

The average cobalt–nitrogen bond length of 1.94 A is in good agreement with previously reported values.[7,8] The mean values of the angles N–N–N and N–Co–N are 105 and 65°, respectively, indicating considerable strain within the chelate ring; the average N–N–N angle in the copper(I) compound was observed to be 116°.[1] The phenyl groups of each ligand group are twisted with respect to one another ($\sim$20°) and with respect to the plane of the triazenido moiety; this provides additional evidence of strain. This situation is distinctly different from that in the copper(I) derivative where it was found that all the atoms of a ligand group are almost exactly coplanar.[1]

There appear to be no significant differences between the nitrogen–nitrogen interatomic distances within any one ligand group; in one case the crystallographic symmetry is such that it demands equivalence of these two bonds. The average value of 1.31 A compares favorably with the value of 1.30 A found for the copper(I) case.[1] This suggests a delocalization of the $\pi$ electrons in the triazenido portion of the ligand. The delocalization could, however, be more extensive because the average nitrogen to phenyl carbon bond length of 1.39 A appears to be significantly shorter than the carbon to nitrogen single-bond length of 1.472 A.[7]

For octahedral complexes, four-membered chelate rings involving three atoms from the first period of the

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periodic table are rare. It has been established that the carbonate, nitrate, acetate, and nitrite ions function as bidentate chelates in the octahedral systems, $[Co(NH_3)_4CO_3]^+$,[8] $[Co(Me_3PO)_2(NO_3)_2]$,[9] zinc acetate dihydrate,[10] and $[Ni(Me_2N(CH_2)_2NMe_2)(NO_2)_2]$,[11] respectively. The cobalt(III) derivative of 1,3-diphenyltriazene appears to provide the first proven example where three four-membered rings are present in the one octahedral coordination sphere.

**Acknowledgment.** We are very grateful to Dr. J. C. B. White for allowing us to use his computer programs.

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**Madeline Corbett, B. F. Hoskins**
*Department of Inorganic Chemistry, University of Melbourne*
*Parkville, N.2., Victoria, Australia*
*Received December 8, 1966*

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## On the Thermodynamic Significance of Delocalization in Dienes. Thermodynamics of the Vinylcyclopropyl System

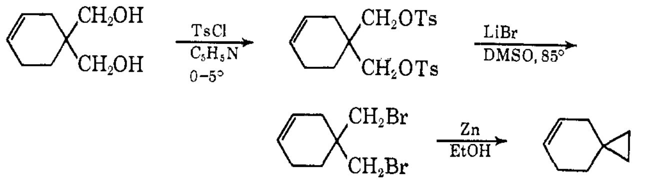
*Sir:*

It has long been known from thermochemical evidence that the heats of formation ($\Delta H_f$) of conjugated[1] compounds, such as dienes, are significantly lower (more stable) than the sum of bond energy terms obtained from saturated or monoolefinic models. The relative importance of the factors contributing to this stabilization (which is generally referred to as the empirical resonance energy) is not clear and has been the subject of considerable discussion in recent years. The commonly accepted interpretation[2] holds that $\pi$ delocalization or resonance accounts for a major portion of this energy difference; more recently, the view[3] has been advanced that delocalization may be relatively unimportant in the ground state of "classical" molecules[4] and that the energy differences can be accounted for on the basis of variations in the binding energy of $\sigma$ bonds as a function of hybridization.

In the absence of a complete and accurate mathematical description of complex molecules, concepts such as hybridization and delocalization can be very useful from a predictive standpoint. In order to clarify the relative thermodynamic importance of these concepts, we have determined the empirical resonance energy of the vinylcyclopropyl system and evaluated it with respect to the known empirical resonance energy of 1,3-butadiene.[5,6]

Interaction of the cyclopropyl group with conjugated $\pi$ systems has been a subject of continuing interest.[7] Recently the geometric consequences of such interactions have been elucidated by nmr,[8] electron diffraction,[9] and kinetic[10] studies. These studies have conclusively established that the minimum energy conformation possesses a "bisected" geometry[11] in which the nodal plane of the adjacent $\pi$ system is normal to the plane of the ring, thus allowing maximum delocalization between the $\pi$ system and the highly p weighted bonds of the cyclopropyl ring. However, although approximate conformational energy differences have been obtained for vinylcyclopropane and closely related compounds,[8a,c-f] and thermochemical studies have been reported for phenyl- and vinylcyclopropane,[7c,12,13] the thermodynamic significance of ground-state interactions in these compounds remains problematical.

We have synthesized spiro[2.5]oct-5-ene (**1**) by the following scheme[14] and have equilibrated both **1** and its conjugated isomer **2**[15] in solutions of *ca.* 1 *N* lithium dimethylamide in hexamethylphosphoramide[16] (LDMA-HMPA) at three different temperatures (see Table I). Equilibrium mixtures were usually obtained in less than 10 min with essentially no decom-



**1** **2**

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[13] The apparent negative resonance energy reported for vinylcyclopropane[7c] is probably not real in light of our present results. Partial polymerization of the combustion sample in transit cannot be discounted: E. J. Prosen, private communication.

[14] (a) This is similar to the scheme of P. Leriverend and J. M. Conia, *Bull. Soc. Chim. France*, 116, 121 (1966). (b) The bromination step is a modification of the procedure of J. Cason and J. S. Correia, *J. Org. Chem.*, **26**, 3645 (1961). All new compounds have been fully characterized by their nmr, infrared, and (for **2**) ultraviolet spectra. Satisfactory analyses were obtained in all cases.

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