A and B are different species and are formed during electrolyses which produce markedly different amounts of ammonia, it is suggested that the mechanism of degradation depends on the applied potential, although dioxygen is always involved.

It is possible that some of the ammonia produced in the degradative reduction of $[\mathrm{Co^{III}(tpps)}]$ is derived from N_2, as has been claimed.[1] Our results suggest that this is not so. Reduction of $[\mathrm{Co^{III}(tpps)}]$ under a 4:1 $(^{15}N)_2:O_2$ mixture produced ammonia with no enrichment of ^{15}N above natural abundance. There was no decrease in ammonia yield when the reduction was carried out under Ar or $Ar:O_2$ instead of air. We also found that when air scrubbed as described was passed through a solution of borohydride and cobalt tris(acetylacetonate) it yielded 0.1 mol NH_3/atom Co. However, when the air was scrubbed with a solution of cobalt tris(acetylacetonate) and sodium borohydride prior to passage through the other traps and test solution, then no detectable amounts of ammonia were produced. Evidently our air contains nitrogenous impurities which are reducible to ammonia and not easily removed by conventional scrubbing techniques.

We conclude that $[\mathrm{Co^{III}(tpps)}]$ does not fix nitrogen under the conditions described[1] and that all the ammonia observed was derived from the combined nitrogen of the ligand.

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Charge Transfer Complexes of Purines and Pyrimidines. 9-Cyclohexyladenine–Iodine in Organic Solvents and in the Solid State

Sir:

The structure and reactivity of nucleic acids is controlled to a large extent by donor–acceptor interactions of the purines and pyrimidines. Yet, in spite of the inherent importance of information about molecular complexes of these compounds, little is known directly about their charge-transfer (CT) interactions. There have been reports that purines and pyrimidines form π complexes with aromatic donors and acceptors such as chloranil, steroids, and the flavines.[1,2] However, weak complexes of these types are undoubtedly stabilized in large part by interactions other than CT forces.[3-5] We report here the first structural and spectral information about a CT complex of a purine which is stabilized primarily by donation of n electrons from a ring nitrogen.

Single crystals of the iodine complex of 9-cyclohexyladenine (CHA) were obtained by allowing iodine to diffuse into a CCl_4 solution of CHA. The unit cell dimensions of the 1:1 complex, $CHA\cdot I_2$, are: $a = 9.1728$ (7), $b = 12.289$ (1), $c = 13.596$ (1) Å; $\beta = 99.564$ (6)°; the space group is $P2_1/c$. A total of 3629 intensity data were used in solving and refining the structure ($R = 0.039$). The iodine forms a CT bond with N(1) of CHA; N(1)···I(1), 2.520 (3) Å and I(1)–I(2), 2.764 (1) Å (Figure 1). Attachment of I_2 at N(1) is an indication that this atom is the most basic ring nitrogen, as is suggested by theoretical charge density calculations[6] and structural observations[7] on protonated adenine derivatives. The CT bond is 0.20–0.25 Å longer than that in the I_2 and ICl complexes of pyridine, 2-picoline, and trimethylamine.[8] The I_2 molecule is not coplanar with the adenine ring, but is inclined to it at an angle of 21.5°. Hydrogen bonding occurs at N(7) and N(10), forming centrosymmetrically related base pairs (Figure 1) of a type not previously observed in crystal structures of self-paired adenine residues. It is interesting to note that this type of pairing has been proposed to account for the stability of the double-stranded helix of polyriboadenylic acid in the low pH range in aqueous media, where N(1) is protonated.[9]

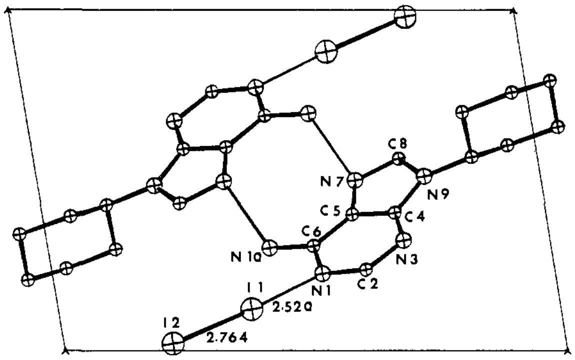

Figure 1. Molecular structure and hydrogen bond pairing in iodine 9-cyclohexyladenine.

The polyiodide solubility method[10] has been used to determine thermodynamic and spectral properties of $CHA\cdot I_2$ in CCl_4. The blue-shifted iodine band of the complex has a maximum absorptivity of 1460 ± 40 l. mol^{-1} cm^{-1} at 415 nm. From measurements of absorbance at the isosbestic point (473 nm) the value of the formation constant (K) is determined to be 186 ± 8 l. mol^{-1}. Spectral properties of the complex are nearly the same in heptane, although owing to the limited solubility of CHA in that solvent, it is difficult to obtain an accurate value of K. A CT band of $CHA\cdot I_2$ is located at 244 nm; it has a peak absorptivity of about 35,000 l. mol^{-1} cm^{-1}. From the frequency of the CT band, an ionization potential of 9.1 eV may be estimated for CHA.[11] All of the spectral and thermodynamic constants determined for $CHA\cdot I_2$ are quite similar to those reported for iodine complexes

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(2) R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, N. Y., 1969, pp 350–351.

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(5) B. Pullman, P. Claverie, and J. Caillet, *Science*, **147**, 1305 (1965).

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(11) H. Yada, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Jap.*, **33**, 1660 (1960); R. S. Mulliken and W. B. Person, *Annu. Rev. Phys. Chem.*, **13**, 107 (1962).

of pyridine and the picolines in organc solvents.[12] At I_2 concentrations greater than about 10^{-3} *M*, there is evidence for the formation of a complex of CHA with two iodine molecules.

Infrared spectra of solutions of CHA and I_2 indicate that the N–H stretching frequencies of the amino group in free CHA (at 3425 and 3540 cm^{-1}) decrease to 3410 and 3525 cm^{-1} in the complex; addition of Br_2 to CHA in CCl_4 produces shifts to 3413 and 3529 cm^{-1}. Frequency shifts of these magnitudes are compatible with the assumed formation of a moderately strong CT bond at N(1), adjacent to the C–NH_2 group of CHA.

The present report clearly indicates the ability of adenine to act as an n donor in forming relatively strong molecular complexes with the halogens. Because of the close relation which exists between the charge density or ionization potential of n donors and the stability, bonding, and structure of their CT complexes, results of the type presented here should find application in investigations of biological systems involving the purines and pyrimidines.

Acknowledgment. This research was supported in part by National Science Foundation Grants GP-23278 and GP-33519X.

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Multiple Condensations with Methyl β-Vinylacrylate

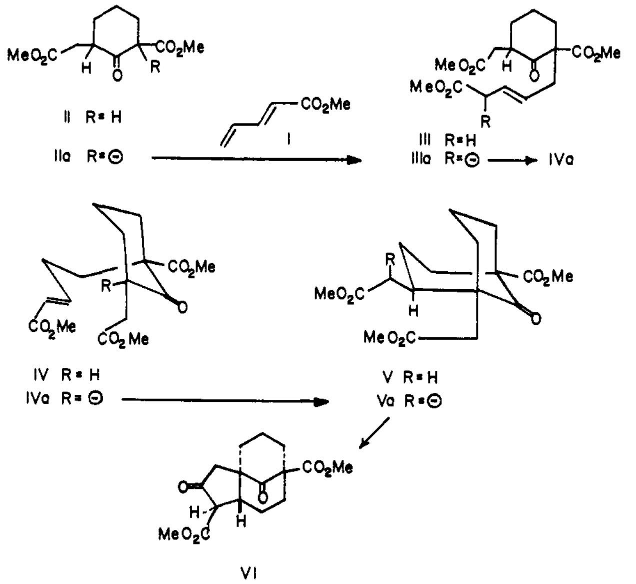
Sir:

Activated butadienes such as I are attacked by nucleophiles in a terminal (1,6-) sense.[1] The multifunctional adducts, so produced, can service subsequent intramolecular processes. Below, we report a *one step* assemblage of the 3a,7-methano-3a*H*-cyclopentacyclooctene system by the condensation of I with II.[2] This process underscores the potentialities of **I** as a multiple annelating agent.

To a solution of 4.8 g (21.5 mmol) of ketodiester II in 150 ml of DMSO was added 7 ml (2.0 mmol) of a stock solution of dimsylsodium.[3] After 15 min 2.5 g (23 mmol) of I was added. An additional 2.0 mmol of base was added after 8 hr and four additional 2.0 mmol increments introduced at 24 hr intervals.[4] At the end of this period,[5] a final 14 mmol increment of base was added (total base = 26 mmol) and stirring continued for an additional 8 hr (total time = 112 hr). Work-up afforded 2.4 g of VI,[6] mp 145–146° (41% yield), and 0.5 g (11%) of recovered II. The entire operation was conducted at room temperature.

In separate experiments, the products of intermediate levels of condensation were obtained in pure form. Thus, using DMSO as solvent and a 0.2 : 1 : 1 ratio of dimsylsodium : I : II for 1.5 hr at room temperature gave an 82% yield of III.[6] When a 1.4 : 1 : 1 ratio of the same reagents was employed for 7 hr at 50°, a 12%[4] yield of bicyclic product V[6] was obtained together with 8% of VI. With pure III and V in hand, the course of the multiple condensation of I + II + B$^-$ → VI was monitored.

Scheme I



The intermediacy of anions IIIa and Va was clearly demonstrated by the formation of III and V, respectively, on quenching after shorter reaction times.[4,5] The intermediacy of IVa would appear to be mechanistically reasonable, though its protonated form, IV, was never detected.

The gross structure and stereochemistry of VI were defined by X-ray diffraction analysis. The compound crystallizes in space group $P2_1/c$ with four molecules per unit cell of the following dimensions: $a = 10.907$ (13), $b = 9.520$ (7), $c = 15.638$ (13) Å; $\beta = 111°\ 49$ (6)′. Intensity data for 2491 independent reflections were measured on a Picker FACS I diffractometer using Cu Kα radiation. Each reflection was scanned 2° in the θ–2θ mode. Lorentz and polarization corrections were made and the data reduced to normalized structure factors (*E*). The signs of the 450 largest *E* values were obtained using the computer program, MULTAN.[7] A fourier synthesis with the phased *E* values as coefficients revealed the 22 nonhydrogen atoms. Hydrogen positions were found in a difference map. The struc-

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[1] (a) E. P. Kohler and F. R. Butler, *J. Amer. Chem. Soc.*, **48**, 1036 (1926); (b) J. W. Ralls, *Chem. Rev.*, **59**, 329 (1959); (c) G. A. Berchtold, J. Ciabattoni, and A. A. Tunick, *J. Org. Chem.*, 30, 3679 (1965); (d) S. Danishefsky and R. Cunningham, *ibid.*, **30**, 3676 (1965); (e) S. Danishefsky and R. Cavanaugh, *ibid.*, **33**, 2959 (1968); (f) S. Danishefsky, G. Koppel, and R. Levine, *Tetrahedron Lett.* 2257 (1968); (g) S. Danishefsky, J. Eggler, and G. Koppel, *ibid*, 4333 (1969); (h) E. J. Corey, C. U. Kim, R. H. K. Chien, and M. Taked, *J. Amer. Chem. Soc.*, **94**, 4395 (1972); (i) F. Näf, P. Degen, and G. Ohloff, *Helv. Chim. Acta*, **55**, 82 (1972).

[2] See F. Ramirez and J. W. Sargent, *J. Amer. Chem. Soc.*, 77, 6297 (1955), for diethyl ester.

[3] E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1353 (1965).

[4] Due to sensitivity of compound I toward base and due to the tendency of III (*via* IIIa) to undergo reversion to I and II with destruction of the former, it is necessary to maintain a low base concentration until III has been transformed to V. At this time,[5] the stoichiometric complement of base, required for the Dieckmann step, may be safely introduced.

[5] At this stage, work-up of an aliquot shows the predominance of V with small amounts of VI and II present. Compound III is no longer observed.

[6] C and H combustion analysis within 0.3% of theory, as well as infrared, nmr, and mass spectra consistent with the proposed structure, were obtained for this compound.

[7] P. Main, *Acta Crystallogr., Sect. A*, 27, 368 (1971).