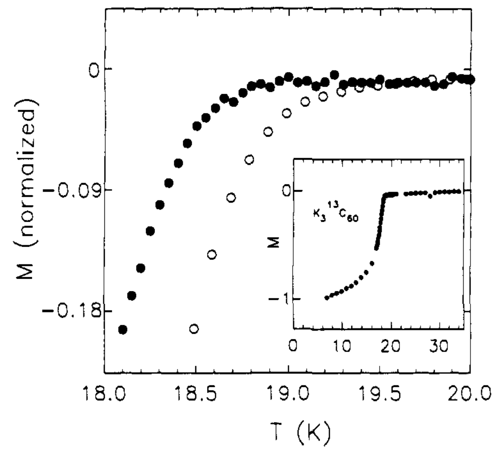

Figure 2. High-resolution temperature-dependent magnetization measurements obtained on $K_3{}^{13}C_{60}$ (●) and $K_3{}^{12}C_{60}$ (○) samples highlighting the depression in T_c for the isotopically substituted material. The samples were initially cooled in zero field to 5 K, and then the curves were recorded on warming in a field of 20 Oe. The curves were normalized to the value of the magnetization at 5 K. The inset shows a full magnetization curve for a $K_3{}^{13}C_{60}$ sample.

addition, we characterized the infrared active modes of $^{13}C_{60}$ and found that the four modes exhibited a classical isotope shift (Table I). These analytical data demonstrate that we prepared isotopically pure $^{13}C_{60}$ and that the purified samples were free from $^{13}C_{70}$ contaminant.

To elucidate the isotope effect on superconductivity, we have studied potassium-doped $^{13}C_{60}$. $K_3{}^{13}C_{60}$ and $K_3{}^{12}C_{60}$ samples were synthesized by heating stoichiometric amounts of solvent-free $^{13}C_{60}$ and $^{12}C_{60}$ with K metal (3:1, K:C_{60}) in sealed quartz tubes (10^{-3} Torr); typically, 1-2 mg of C_{60} was used.[9] The temperature was ramped from 200 to 400 °C over a 1-week period during the reaction.[10,11] $K_3{}^{13}C_{60}$ and $K_3{}^{12}C_{60}$ samples were prepared simultaneously in the same furnace to minimize differences due to the preparative conditions.

Typical temperature-dependent shielding magnetization data obtained from $K_3{}^{13}C_{60}$ and $K_3{}^{12}C_{60}$ samples using a SQUID-based magnetometer (MPMS2, Quantum Design, San Diego, CA) are shown in Figure 2. The full shielding curve for $K_3{}^{13}C_{60}$ (Figure 2, inset) exhibits a sharp transition with an onset at 18.8 K; sharp transition onsets are also observed for the $K_3{}^{12}C_{60}$ samples. The rounding in the low-temperature data is expected since the grain size of these polycrystalline materials is similar to the magnetic penetration depth; similar broadening is observed in the $K_3{}^{12}C_{60}$ results obtained in this study and reported elsewhere.[5,10] Since the transition onsets are sharp in both the $K_3{}^{13}C_{60}$ and $K_3{}^{12}C_{60}$ curves, we assign T_c as the onset temperature of diamagnetic shielding.[12] The key experimental result of this study shown in Figure 2 is the depression of T_c from 19.2 K for $K_3{}^{12}C_{60}$ to 18.8 K for isotopically pure $K_3{}^{13}C_{60}$. Our analytical data indicate it is unlikely that the decrease in T_c for $K_3{}^{13}C_{60}$ is due to impurities, and thus we attribute the shift in T_c to a true mass effect. Taking into account the uncertainty in all of our data, we find that $\Delta T_c = 0.45 \pm 0.1$ K. Since these data are obtained on isotopically pure compounds, they represent unambiguously the $^{13}C/^{12}C$ isotope effect on T_c.

It is important to compare the observed depression of T_c for isotopically pure $K_3{}^{13}C_{60}$ material with different models of superconductivity. Conventional Bardeen-Cooper-Schrieffer (BCS) theory predicts an isotope effect of $T_c \propto M^{-\alpha}$, where M is the ionic mass and $\alpha = 0.5$.[3] Using the value of ΔT_c determined above we find that $\alpha = 0.3 \pm 0.06$. This experimentally determined value of α places important constraints on the mechanism of superconductivity. First, the observation of the isotope effect strongly suggests that pairing mechanisms involving only electronic interactions are unlikely for these new materials.[1] Secondly, while it is apparent that phonons are important, the value of α indicates that the standard BCS model must be modified to account for superconductivity in the fullerenes. Since a similar value of α is deduced from studies of incompletely ^{13}C-substituted Rb_3C_{60} ($\alpha = 0.37$),[5] we believe that this conclusion is robust. It is known from studies of conventional superconductors that strong coupling can reduce the value of α from the BCS limit of 0.5.[13,14] Interestingly, our recent tunneling measurements on K_3C_{60} and Rb_3C_{60}[15] and theoretical calculations[16] have indicated that these may be strong coupling superconductors.

Acknowledgment. We thank A. N. Tyler for the mass spectroscopy measurements, D. W. Murphy for communication of unpublished results, D. R. Huffman and W. Kratschmer for helpful discussions, and J. L. Huang for technical assistance. C.M.L. acknowledges support of this work by the David and Lucile Packard Foundation and the NSF Presidential Young Investigator Program. The NMR and mass spectroscopy facilities are supported by grants from the NIH and NSF.

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[11] Fleming, R. M.; Ramirez, A. P.; Rosseinsky, M. J.; Murphy, D. W.; Haddon, R. C.; Zahurak, S. M.; Makhija, A. V. *Nature* **1991**, *352*, 787.

[12] The value of T_c determined this way for $K_3{}^{12}C_{60}$, 19.2 K, agrees well with previous reports.[10,11]

[13] (a) Morel, P.; Anderson, P. W. *Phys. Rev.* **1962**, *125*, 1263. (b) McMillan, W. L. *Phys. Rev.* **1968**, *167*, 331.

[14] The change in lattice constant on isotopic substitution will also affect T_c;[5] we are currently investigating this contribution.

[15] (a) Zhang, Z.; Chen, C.-C.; Lieber, C. M. *Science* **1991**, *254*, 1619. (b) Zhang, Z.; Chen, C.-C.; Kelty, S. P.; Dai, H.; Lieber, C. M. *Nature* **1991**, *353*, 333.

[16] Erwin, S. C.; Pickett, W. E. *Science* **1991**, *254*, 842.

New Approaches to the Generation of Phosphinidenes

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The chemistry of phosphinidenes (phosphanediyls, RP) is much less developed than that of carbenes, nitrenes, and silylenes. Evidence for the intermediacy of phosphinidenes has been adduced from metal-promoted dehalogenation of dihalophosphines, cyclopolyphosphine thermolysis, diphosphene photolysis, and various cycloreversion reactions.[1] However, in many of these cases, it is possible to devise alternative trapping mechanisms that do not involve a phosphinidene.[1c] It occurred to us that, as in the case of nitrenes,[2] for example, phosphinidenes might be generated more efficiently by elimination of thermodynamically stable molecules such as N_2 and CO from suitable precursors.

Polyazides of phosphorus(V) are well known;[3] however, $P(N_3)_3$ is reported to be very unstable[4] and, in fact, isolable phosphorus(III) azides are confined to mono(azides) of the general type

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[1] For reviews, see: (a) Schmidt, U. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 523. (b) Weber, B.; Regitz, M. In *Houben-Weyl, Methoden der Organischen Chemie*; Thieme: Stuttgart, 1982; Vol. E1. (c) Mathey, F. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Thieme: Stuttgart, 1990. See also: (d) Bock, H.; Bankmann, M. *J. Chem. Soc., Chem. Commun.* **1989**, 1130. (e) Yoshifuji, M.; Sato, T.; Inamoto, N. *Chem. Lett.* **1988**, 1735.

[2] See, for example: Bock, H.; Dammel, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 506. Bock, H.; Breuer, O. *Ibid.* **1987**, *26*, 461.

[3] For reviews, see: Fluck, E. *Top. Phosphorus Chem.* **1967**, *4*, 291. Cremlyn, R. J. W.; Wakeford, D. H. *Ibid.* **1976**, *8*, 1. See also: Dillon, K. B.; Platt, A. W. G.; Waddington, T. C. *J. Chem. Soc., Dalton Trans.* **1981**, 2292.

[4] Dillon, K. B.; Platt, A. W. G.; Waddington, T. C. *J. Chem. Soc., Dalton Trans.* **1980**, 1036.

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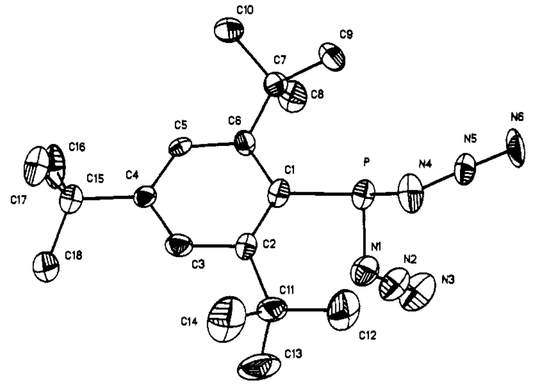
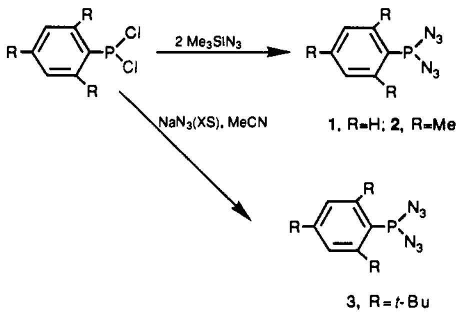


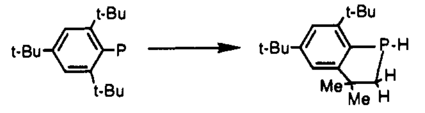
Figure 1. ORTEP view of **3**. Selected distances (Å) and angles (deg): P-N1, 1.737 (8); N1-N2, 1.23 (1); N2-N3, 1.12 (1); P-N4, 1.733 (9); N4-N5, 1.21 (1); N5-N6, 1.10 (1); C1-P-N1, 99.7 (4); N1-P-N4, 102.0 (4); C1-P-N4, 103.5 (4); P-N1-N2, 116.2 (8); P-N4-N5, 120.6 (8).

R_2PN_3 (R = Ph, CF_3, amido).[5] Since the thermolysis or photolysis of phosphorus(III) mono(azides) results in a variety of products with phosphorus–nitrogen bonds,[5] such compounds are unsuitable as phosphinidene precursors. We therefore focused our attention on bis(azides) of the type $RP(N_3)_2$. We have isolated the first examples of this class of compound by the routes summarized below:



Compound **1** is very unstable, and decomposition takes place prior to the completion of the reaction of $PhPCl_2$ with Me_3SiN_3. We were, however, able to detect a ^{31}P NMR chemical shift for **1**.[6] The bis(azide) **2** is a bright yellow-orange oil which is stable for a few hours in solution.[6] Interestingly, **3** is a colorless solid which is stable in air; it has been characterized spectroscopically[6] and by X-ray analysis (Figure 1).[7] The UV spectrum of **3** comprises a broad absorption band which extends from 210 to 330 nm with λ_{max} at 223 nm ($\epsilon = 14\,000$ M^{-1} cm^{-1}). Thus far, we have not experienced any difficulties in handling **1–3**. However, *great caution should be exercised* because the percent weights of nitrogen in **1**, **2**, and **3** are 43.7, 35.9, and 23.3%, respectively.[8]

Photolysis of **2** with 254-nm light results in the formation of (mesityl $P)_{4,5}$, while photolysis in the presence of excess Me_2S_2 (**4**) converts **2** to (mesityl)$P(SMe)_2$ (**5**).[6] The formation of **5** is suggestive of the insertion of triplet (mesityl)P into the sulfur-sulfur bond of **4**. However, more convincing evidence for phosphinidene intermediacy (**6**) stems from the photolysis of **3** with 254-nm light, which results in conversion to the phosphaindan **7**.[9]



6 **7**

No deuterium incorporation is observed when the photolysis is conducted in deuterated solvents, thus implying that the rearrangement of **6** to **7** is intramolecular. The ground state of **6** is almost certainly a triplet. Theoretical studies indicate that the ground states of HP[10] and CH_3P[11] are triplets; moreover, the triplet–singlet energy gap of HP has been established experimentally to be 21.9 kcal/mol.[12] In collaborative theoretical work (Gaussian 88, 6-31G* basis set),[13] we have established that the $^3A_2$ state of the model arylphosphinidene C_6H_5P is more stable than the $^1A_1$ state by between 45.4 and 57.5 kcal/mol, depending on whether ROHF or UHF orbitals, respectively, are employed.

The electronic spectrum of the phosphaketene (2,4,6-*t*-$Bu_3C_6H_2$)P=C=O (**8**)[14] exhibits absorptions at 250, 286, and 472 nm. The irradiation of **8** with either 254-nm or 300-nm light causes quantitative conversion to the phosphaindan **7**.[15] We have found that photolysis (254 nm) of **8** in the presence of excess S_8 in toluene produced the known[16] dithiophosphorane (2,4,6-*t*-$Bu_3C_6H_2)PS_2$. On the basis of spin conversion, rupture of the phosphorus–carbon bond of **8** is anticipated to produce both **6** and CO in their singlet states. By analogy with arylnitrenes,[17] intersystem crossing to the triplet state of **6** can be postulated. Indeed, irradiation of **8** at 320 nm with a tunable dye laser revealed intermediates with lifetimes of 8.29×10^{-7} and 5.25×10^{-6} s.[18]

Finally, we note that the reaction of **8** with Et_2NH takes place in the dark, results in (2,4,6-*t*-$Bu_3C_6H_2)P(NEt_2)H$, and thus does not involve the phosphinidene intermediate. It has been argued previously[14,19] that the polarity of the phosphorus–carbon bond of phosphaketenes is $P^{\delta-} = C^{\delta+}$; hence, a reasonable mechanism for the Et_2NH reaction is nucleophilic attack at carbon by Et_2N^-, protonation at phosphorus, followed by 1,2 migration of the amido group and elimination of CO.

Acknowledgment. We thank the National Science Foundation

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(5) Bertrand, G.; Majoral, J.-P.; Baceiredo, A. *Acc. Chem. Res.* **1986**, *19*, 17 and references therein.

(6) ^{31}P NMR (121.5 MHz, C_6D_6, 295 K, 85% H_3PO_4 ext.): **1**, δ 125; **2**, δ 138; **3**, δ 132; **5**, δ 92. ^1H NMR (300.15 MHz, C_6D_6, 295 K, TMS ext.): **3**, δ 1.19 (s, 9 H, *p*-$(CH_3)_3C$), 1.52 (s, 18 H, *o*-$(CH_3)_3C$), 7.46 (d, 2 H, $^4J_{PH}$ = 2.70 Hz, H-aryl); **5**, δ 2.43 (d, 6 H, $^3J_{PH}$ = 14.90 Hz, CH_3S), 2.49 (s, 3H, *p*-CH_3), 2.62 (s, 6 H, *o*-CH_3), 7.01 (s, 2 H, H-aryl). $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6, 295 K, TMS ext.) δ 31.03 (s, *p*-$(CH_3)_3C$), 34.99 (s, *p*-$(CH_3)_3C$), 34.04 and 34.15 (s, *o*-$(CH_3)_3C$), 39.65 and 39.68 (s, *o*-$(CH_3)_3C$), 124.06 (d, $^3J_{PC}$ = 5.96 Hz, *m*-C aryl), 131.30 (d, $^1J_{PC}$ = 45.27 Hz, *ipso*-C), 152.80 (s, *p*-C aryl, 158.26 (d, $^2J_{PC}$ = 16.32 Hz, *o*-C aryl). IR: **3**, ν_{asym} (N_3) 2110, 2160 cm^{-1}, ν_{sym} (N_3) 1280, 1320 cm^{-1}. MS (EI, 70 eV): **3**, *m/e* 276 ($M^+ - 6N$), 261 ($M^+ - 6N - Me$), 246 ($M^+ - 6N - 2Me$), 231 ($M^+ - 6N - 3Me$), 220 ($M^+ - 6N - t$-Bu), 205 ($M^+ - t$-Bu $-$ Me), 164 ($M^+ - 2t$-Bu + 2H); **5**, *m/e* 244 (M^+), 229 ($M^+ - CH_3$), 197 ($M^+ - SCH_3$), 181 ($M^+ - SCH_3 - CH_4$), 149 ($M^+ - 2SCH_3 - H$). MS (CI, CH_4): **3**, *m/e* 361 ($M^+ + H$), 345 ($M^+ - N - H$), 318 ($M^+ - 3N$), 305 ($M^+ - 4N + H$), 290 ($M^+ - 5N$), 277 ($M^+ - 6N + H$). HRMS (CI): **3** for $C_{18}H_{30}N_6P_1$ ($M^+ + H$) calcd 361.2269, found 361.2259. HRMS (EI): **5** for $C_{11}H_{17}PS_2$ (M^+) calcd 244.0509, found 244.0501.

(7) Crystal data for **3** ($C_{18}H_{29}N_6P$): orthorhombic, space group *Pbca* with a = 11.413 (3), b = 19.251 (4), c = 18.638 (3) Å, V = 4095 (2) Å^3, Z = 8, d_{calcd} = 1.17 g cm^{-3}, μ (Mo Kα) = 1.24 cm^{-1}. A total of 2521 reflections was collected at 298 K on an Enraf Nonius CAD-4 diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71069 Å) and the $\theta/2\theta$ scan mode. The structure of **3** was solved by direct methods and refined (full-matrix, least-squares) to a final R value of 0.0496.

(8) The empirical lower limit for the explosivity of covalent azides is 25% by weight azide nitrogen. Patai, S., Ed. *The Chemistry of the Azide Group*; Interscience: London, 1971.

(9) This compound has been synthesized previously by an independent route: Cowley, A. H.; Pakulski, M. *Tetrahedron Lett.* **1984**, *25*, 2125. The conversion of **3** to **7** can also be effected by vapor phase thermolysis at 300 °C.

(10) Mavridis, A.; Harrison, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 7651. Trinquier, G. *Ibid.* **1982**, *104*, 6969.

(11) Nguyen, M. T.; McGinn, M. A.; Hegarty, A. F. *Inorg. Chem.* **1986**, *25*, 2185.

(12) Zittel, P. F.; Lineberger, W. C. *J. Phys. Chem.* **1976**, *65*, 1236.

(13) Boggs, J. E.; Willetts, A.; Cowley, A. H. To be published.

(14) Appel, R.; Paulen, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 785; *Tetrahedron Lett.* **1983**, *24*, 2639.

(15) See also: Appel, R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Thieme: Stuttgart, 1990.

(16) Appel, R.; Knoch, F.; Kunze, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1004. Navech, J.; Majoral, J.-P.; Kraemer, R. *Tetrahedron Lett.* **1983**, *24*, 5885. Yoshifuji, J.; Toyota, K.; Ando, K.; Inamoto, N. *Chem. lett.* **1984**, 317.

(17) Leyva, E.; Platz, M. S. *Tetrahedron Lett.* **1985**, *26*, 2147. Li, Y. Z.; Kirby, J. P.; George, M. W.; Poliakoff, M.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 8092 and references therein.

(18) Quantel, Q-Switched Nd/YAG laser, 10-ns pulse, CH_3CN solution.

(19) Nguyen, M. T.; Hegarty, A. F.; McGinn, M. A.; Ruelle, P. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1991.

and the Robert A. Welch Foundation for generous financial support.

Supplementary Material Available: Tables of bond distances, bond angles, atomic coordinates, and thermal parameters for **3** (6 pages); listings of observed and calculated structure factors for **3** (6 pages). Ordering information is given on any current masthead page.

Novel Interstrand Cross-Links Induced by the Antitumor Antibiotic Carzinophilin/Azinomycin B

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Carzinophilin is an antitumor antibiotic isolated from the culture broth of *Streptomyces sahachiroi*,[1] whose structure determination has remained elusive for over 30 years.[2,3] Comparison of carzinophilin with azinomycin B, a recently[4] isolated metabolite from *Streptomyces griseofuscus* S42227, confirms that they are the same compound.[5] Earlier studies concluded that carzinophilin caused significant DNA damage both in vitro and in vivo as a result of cross-link formation.[6] We wish to report that bifunctional alkylation by carzinophilin[7] affords interstrand cross-links in the major groove between G and purine residues two bases removed in duplexed DNA fragments containing the sequences

5′-GNT-3′ 5′-GNC-3′
3′-CNA-5′ 3′-CNG-5′

We reached this conclusion by the rational design of synthetic oligonucleotides containing the bases inosine and 7-deazaguanine at the target alkylation sites.

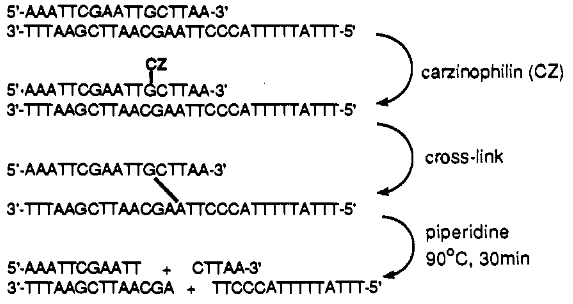
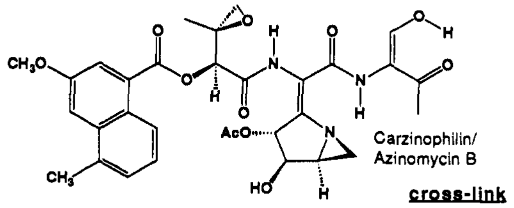


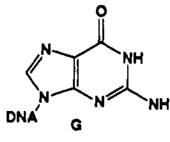
Figure 1.

Table I. Relative Efficiency of Interstrand Cross-Link Formation of Duplex DNAs **1–10** Following Incubation with Carzinophilin/Azinomycin B (* Denotes Trace). All Duplexes Are Identical Except for Variations in the Highlighted Three Base Pair Sequence

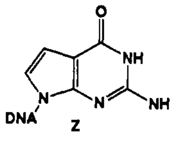


Carzinophilin/
Azinomycin B

		cross-link
1.	12 13 14 5'-AAATTCGAATT GCT TAA-3' 3'-TTTAAGCTTAA CGA ATTCCCATTTTTATTT-5' 19 18 17	++
2.	5'-AAATTCGAATT ZCT TAA-3' 3'-TTTAAGCTTAA CGA ATTCCCATTTTTATTT-5'	0
3.	5'-AAATTCGAATT GCT TAA-3' 3'-TTTAAGCTTAA CZA ATTCCCATTTTTATTT-5'	+
4.	5'-AAATTCGAATT ICT TAA-3' 3'-TTTAAGCTTAA CGA ATTCCCATTTTTATTT-5'	+
5.	5'-AAATTCGAATT GCT TAA-3' 3'-TTTAAGCTTAA CIA ATTCCCATTTTTATTT-5'	++
6.	5'-AAATTCGAATT GAT TAA-3' 3'-TTTAAGCTTAA CTA ATTCCCATTTTTATTT-5'	0*
7.	5'-AAATTCGAATT GTT TAA-3' 3'-TTTAAGCTTAA CAA ATTCCCATTTTTATTT-5'	0*
8.	5'-AAATTCGAATT GCC TAA-3' 3'-TTTAAGCTTAA CGG ATTCCCATTTTTATTT-5'	++
9.	5'-AAATTCGAATT GAC TAA-3' 3'-TTTAAGCTTAA CTG ATTCCCATTTTTATTT-5'	+
10.	5'-AAATTCGAATT GCA TAA-3' 3'-TTTAAGCTTAA CGT ATTCCCATTTTTATTT-5'	0*



G



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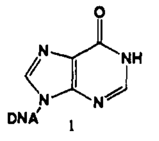

I

Incubation of carzinophilin (11 °C, pH 7, 24 h) with duplex DNA **1** (Table I), ^{32}P-end-labeled at the 5′ terminus of the long or the short strand[8] followed by denaturing polyacrylamide gel electrophoresis (PAGE) analysis, afforded bands of higher molecular weight (lower gel mobility), which were identified as

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(1) Hata, T.; Koga, F.; Sano, Y.; Kanamori, K.; Matsumae, A.; Sugawara, R.; Shima, T.; Ito, S.; Tomizawa, S. *J. Antibiot., Ser. A* **1954**, *7*, 107. All experiments were conducted with carzinophilin from *S. sahachiroi*. The structure of carzinophilin shown in this paper was proposed by Nakashima for azinomycin B (ref 4).

(2) Initial decomposition fragments: Onda, M.; Konda, Y.; Omura, S.; Hata, T. *Chem. Pharm. Bull.* **1971**, *19*, 2013. For other structures, see: Lown, J. W.; Hanstock, C. C. *J. Am. Chem. Soc.* **1982**, *104*, 3213. Onda, M.; Konda, Y.; Hatano, A.; Hata, T.; Omura, S. *J. Am. Chem. Soc.* **1983**, *105*, 6311. Onda, M.; Konda, Y.; Hatano, A.; Hata, T.; Omura, S. *Chem. Pharm. Bull.* **1984**, *32*, 2995.

(3) Synthetic approaches to CZ have generated partial fragments which correlate well with spectral data of the natural product, although ultimate confirmation of the structure will have to await total synthesis or X-ray analysis. For initial studies, see: Shibuya, M. *Tetrahedron Lett.* **1983**, *24*, 1175. Garner, P. *Tetrahedron Lett.* **1984**, *25*, 5855. Garner, P.; Park, J. M.; Rotello, V. *Tetrahedron Lett.* **1985**, *26*, 3299. More recently, partial fragments containing the epoxide of structure **1** have been synthesized: Shibuya, M.; Terauchi, H. *Tetrahedron Lett.* **1987**, *28*, 2619. Ando, K.; Yamada, T.; Shibuya, M. *Heterocycles* **1989**, *29*, 2209. England, P.; Chun, K.-H.; Moran, E. J.; Armstrong, R. W. *Tetrahedron Lett.* **1990**, *31*, 2669. Moran, E. J.; Armstrong, R. W. *Tetrahedron Lett.* **1991**, *32*, 3807.

(4) Yokoi, K.; Nagaoka, K.; Nakashima, T. *Chem. Pharm. Bull.* **1986**, *34*, 4554. Ishizeki, S.; Ohtsuka, M.; Irinoda, K.; Kukita, K.-I.; Nagaoka, K.; Nakashima, T. *J. Antibiot.* **1987**, *40*, 60. Nagaoka, K.; Matsumoto, M.; Oono, J.; Yokoi, K.; Ishizeki, S.; Nakashima, T. *J. Antibiot.* **1986**, *34*, 1527.

(5) Armstrong, R. W.; Salvati, M. E.; Moran, E. J. Submitted for publication.

(6) Terawaki, A.; Greenberg, J. *Biochim. Biophys. Acta* **1966**, *119*, 59. Terawaki, A.; Greenberg, J. *Nature* **1966**, *209*, 481. Lown, J. W.; Begleiter, A.; Johnson, D.; Morgan, A. R. *Can. J. Biochem.* **1976**, *54*, 110.

(7) Formation of identical cross-links were observed for the drug derived from both *S. sahachiroi* (carzinophilin) and *S. griseofuscus* (azinomycin).

(8) Duplex **1** was designed to probe the competitive formation of G-to-G cross-links involving G residues which are either 3′ or 5′ diagonally-substituted. To facilitate the identification of potential cross-links, DNA strands of differing lengths were chosen since only interstrand cross-links should coelute when either strand is separately radiolabeled. This procedure readily differentiates between intrastrand reactions or strand modifications (multiple alkylations) which might also result in bands of decreased mobility by denaturing PAGE analysis. Complementary DNA strands were synthesized on an Applied Biosystems Model 381A synthesizer and were purified as detritylated oligomers using an Axxi-Chrom ODS column (10–15% CH_3CN gradient in a 0.1 M triethylammonium acetate solution at pH 7).

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