adhered to reasonably well in the closo boranes and carboranes but does not apply as generally to the open boranes.[7b]

Atom B_{11} is an extraordinary fractional center, having five cage bonds and one external B–H_t bond. Also, B7 in $B_{16}H_{20}$ (charge 0.12) receives about 0.2 e from the 1,2,3 bond, supporting the ideas above. As noted for B_4H_{10},[13b] the usual two- and three-center bonds may become multicentered below a level of about 0.2 e donation.

We have recently completed PRDDO–Boys LMO studies on other large boron hydrides.[14] Normal-$B_{18}H_{22}$ yields two $B_{10}H_{14}$ fragment structures which have the same LMO bonding as that found for the $B_{10}H_{14}$ fragment in $B_{16}H_{20}$. Also, $B_{20}H_{18}^{2-}$ localizes to a regular three-center structure, and $B_{20}H_{16}$ localizes to a structure which preserves D_{2d} symmetry. *i*-$B_{18}H_{22}$ yields a slightly irregular structure and photo-$B_{20}H_{18}^{2-}$ shows multiple maxima on the localization surface.

An LMO structure for $B_{16}H_{20}$ constructed from the LMO's of $B_{10}H_{14}$ and B_8H_{12} is closely related to the correct LMO structure. This result, and similar results for other molecules, indicates substantial transferabilities of LMO's from smaller molecules to closely related regions of larger molecules. However, the LMO's do depend on the overall charge distribution. If the charge distributions in the smaller molecules are not similar to those in the appropriate region of the larger molecule, then complete transferability does not occur.

The results obtained here from PRDDO–Boys LMO's are consistent with bridging of icosahedral fragments in large boron hydrides, and they also clarify fractional bonding and simplify results on the topological theory.[15]

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(14) D. A. Dixon, D. A. Kleier, T. A. Halgren, and W. N. Lipscomb, to be submitted for publication.
(15) (a) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963; (b) W. N. Lipscomb, *Accounts Chem. Res.*, **6**, 257 (1973); (c) I. R. Epstein and W. N. Lipscomb, *Inorg. Chem.*, **10**, 1921 (1971).

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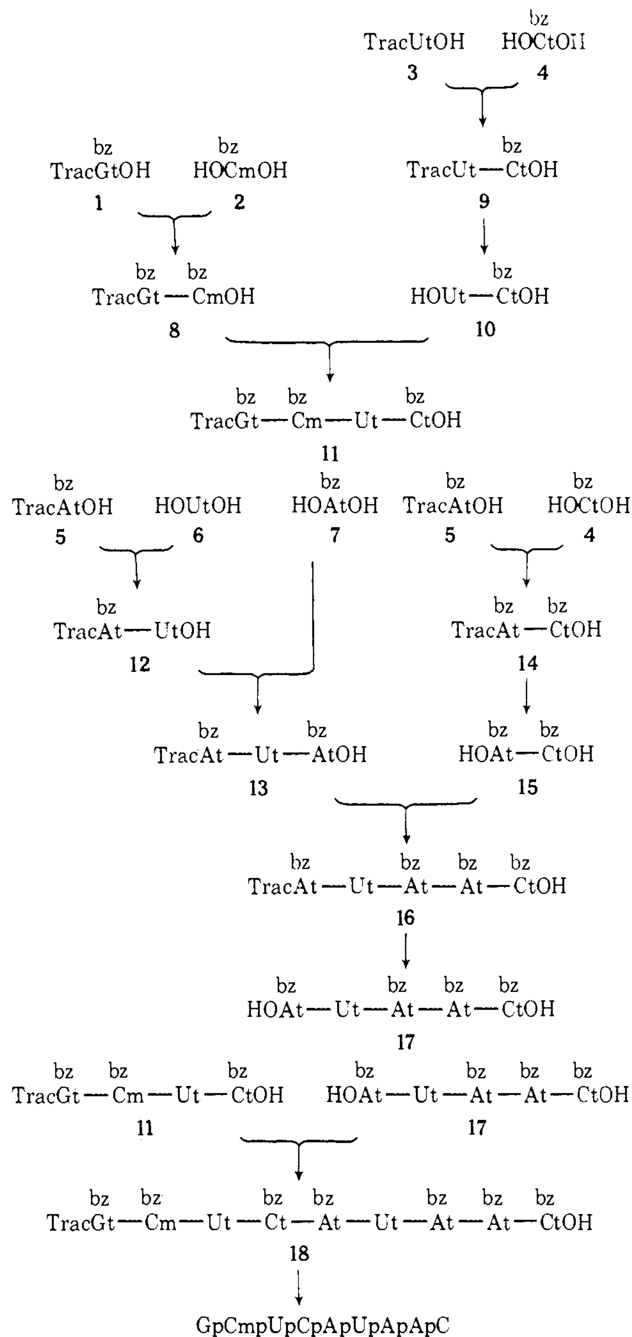
Synthesis of the Anticodon Loop of *Escherichia coli* Methionine Transfer Ribonucleic Acid[1]

Sir:

Large scale synthesis of oligoribonucleotides corresponding to discrete sequences within native ribonucleic acids should encourage further studies in protein–nucleic acid recognition. One such chemical synthesis, the duplex stem region of yeast $tRNA^{Ala}$, has

(1) Communication constitutes Paper VII in a series entitled "Oligoribonucleotide Synthesis." Part VI: E. S. Werstiuk and T. Neilson, *Can. J. Chem.*, **51**, 1889 (1973).

Scheme I



been carried out[2] using a modification of the established phosphodiester method.[3]

We now report the synthesis of the nonaribonucleotide, GpCmpUpCpApUpApApC, which corresponds to the anticodon loop of $tRNA_f^{Met}$ from *E. coli*,[4] using the recently developed phosphotriester fragment coupling method.[5] A summary is shown in Scheme I.[6] Oligonucleotide synthesis using intermediates containing

(2) E. Ohtsuka, M. Ubasawa, S. Morioka, and M. Ikehara, *J. Amer. Chem. Soc.*, **95**, 4725 (1973).
(3) R. Lohrmann, D. Söll, H. Hayatsu, E. Ohtsuka, and H. G. Khorana, *J. Amer. Chem. Soc.*, **88**, 819 (1966).
(4) S. K. Dube, K. A. Marcker, B. F. C. Clark, and S. Cory, *Nature (London)*, **218**, 232 (1968).
(5) E. S. Werstiuk and T. Neilson, *Can. J. Chem.*, **50**, 1283 (1972).
(6) Abbreviations are as suggested by the IUPAC–IUB commission, *Biochemistry*, **9**, 4022 (1970). Trac is 5′-*O*-triphenylmethoxyacetyl, t is 2′-*O*-tetrahydropyranyl, and m is 2′-*O*-methyl. Hyphen between two characters, *e.g.*, At-Ut, indicates a 2,2,2-trichloroethyl phosphotriester internucleotide linkage.

Table I

	Reactants					Product	
No.	Quantity (mmol)		No.	Quantity (mmol)		No.	Quantity (%)
1	400 mg (0.54)	+	**2**	288 mg (0.80)	→	**8**	450 mg (62)
3	500 mg (0.88)	+	**4**	555 mg (1.3)	→	**9**	727 mg (68)
8	110 mg (0.083)	+	**10**	118 mg (0.125)	→	**11**	50 mg (24)
5	1.10 g (1.46)	+	**6**	705 mg (2.19)	→	**12**	1.4 g (75)
12	1.4 g (1.09)	+	**7**	760 mg (1.65)	→	**13**	1.4 g (66)
5	800 mg (1.06)	+	**4**	700 mg (1.62)	→	**14**	950 mg (68)
13	1.4 g (0.72)	+	**15**	1.17 g (1.08)	→	**16**	910 mg (39)
11	50 mg (0.020)	+	**17**	58 mg (0.020)	→	**18**	23 mg (21)
9	350 mg				→	**10**	180 mg (68)
14	426 mg				→	**15**	130 mg (39)
16	200 mg				→	**17**	60 mg (33)

Table II[a]

Free oligonucleotides	Yield, %	R_{Gp} Pc	Tlc	Pe	Enzymic analysis
GCm	71	1.54	1.37	0.29	G:Cm (0.95:1.0)
UC	73	1.30	1.47	0.49	C:U (1.0:1.0)
GCmUC	80	0.61	0.86	0.82	G:Cm:C:U (1.0:1.1:1.1:1.0)
AUA	85	0.88	1.26	0.55	A:U (2.1:1.0)
AC	85	1.56	1.70	0.27	A:C (1.0:1.0)
AUAAC	81	0.70	0.81	0.88	A:C:U (3.1:1.1:1.0)
GCmUCAUAAC	70	0.18	0.15	0.89	G:Cm:A:C:U (1.0:1.1:2.9:1.1:1:0)
Gp		1.0	1.0	1.0	
U				0.0	

[a] Paper chromatography (pc) and thin layer chromatography (tlc) were carried out using Whatman No. 1 (descending method) and Avicel cellulose plates, respectively, in 1-propanol–concentrated ammonia–water solvent (55:10:35, v/v). Bovine spleen diesterase products were compared with authentic markers in the same system. Paper electrophoresis was performed at 1400 V/66 cm using Whatman 3 MM paper and 0.05 *M* triethylammonium bicarbonate, pH 8.0.

phosphotriester nucleotide linkages is now recognized as offering many advantages,[7] especially scale. The present procedure gives nonaribonucleotides in milligram amounts.

Protected ribonucleosides (**1–7**) to be used as building blocks were available.[1,5,8] Protected di- or triribonucleotides (**8**, **9**, **13**, and **14**) were assembled stepwise from their 5′-termini starting with 5′-trityloxyacetyl nucleosides. Block phosphotriester synthesis of nonaribonucleotide derivative **18** was accomplished using a similar procedure from protected tetranucleotide **11** and pentanucleotide **17** which had been the coupling products of dinucleotide derivatives **8** and **10** and of trinucleotide **13** and dinucleotide derivative **15**, respectively.

Experimental data are summarized in Table I. Phosphotriester coupling was carried out in a two-step procedure.[9] In a typical experiment, protected 5′-trityloxyacetyl nucleoside or oligomer (1 equiv) was condensed completely with 2,2,2-trichloroethyl phosphate[10] (2 equiv) in anhydrous pyridine using triisopropylbenzenesulfonyl chloride (TPS) (4 equiv) in 1–2 days at ambient temperatures. Reaction was monitored using silica gel tlc in 10% CH_3OH–CH_2Cl_2: R_f 0.85–0.75 → 0.1. Methylene chloride extraction of the quenched reaction gave the 3′-phosphate derivative as its pyridinium salt which was reactivated with TPS (2 equiv) in anhydrous pyridine and condensed completely with the 5′-hydroxyl of the next protected nucleoside or dinucleoside monophosphate (1–2 equiv) in 2–5 days (R_f 0.1 → 0.8–0.7). Methylene chloride extraction of the quenched reaction gave the crude oligomer which was purified by silica gel column chromatography in methylene chloride using increasing percentages of methanol in methylene chloride as eluent. Column progress was monitored by tlc. Yields of protected oligomer were satisfactory for couplings of single nucleosides (>50%) but were lower (20–30%) for couplings involving fragments. These yields represent an improvement over the earlier synthesis[2] whose stepwise and fragment couplings were approximately 20 and 10%, respectively, frequently using tenfold excess of one reactant. Trityloxyacetate protection offered two major advantages. Compounds containing this grouping can be detected in minute amounts as yellow colorations by ceric sulfate spray on tlc plates. Mild alkaline treatment (0.15 *N* NH_3 in methanol) provides selective deblocking of 5′-hydroxyl groups and was used for the conversion of **9**, **14**, and **16** to **10**, **15**, and **17**, respectively.

Complete deblocking[9] to give free oligonucleotides was carried out on key intermediates, as well as **18**, in good yield. A three-step procedure was used. (a) Reductive cleavage by a Cu–Zn couple[10] in DMF for 1 day at 50°, removed all 2,2,2-trichloroethyl groups[9] from the phosphate residues. (b) Ammonolysis of benzamide and trityloxyacetyl groups was accomplished in 7 *N* ammonia for 2 days at ambient temperatures. (c) Acidic hydrolysis (pH 2) for 1 day at 22° removed the tetrahydropyranyl groups without any detectable phosphate isomerization.[8a] Spleen diesterase analyses gave acceptable ratios of the parent 3′-nucleotides and nucleosides as shown in Table II.

Meaningful anticodon–codon recognition studies will require GpCmpUpCpApUpApApC to adopt the

(7) J. C. Catlin and F. Cramer, *J. Org. Chem.*, **38**, 245 (1973).
(8) (a) B. E. Griffin, M. Jarman, and C. B. Reese, *Tetrahedron*, **24**, 639 (1968); (b) T. Neilson and E. S. Werstiuk, *Can. J. Chem.*, **49**, 493 (1971); (c) T. Neilson, E. V. Wastrodowski, and E. S. Werstiuk, *ibid.*, **51**, 1068 (1973). Preparation of **2** will be described elsewhere.
(9) T. Neilson and E. S. Werstiuk, *Can. J. Chem.*, **49**, 3004 (1971).
(10) F. Eckstein, *Chem. Ber.*, **100**, 2228 (1967).

correct conformation.[11] Syntheses of longer oligonucleotides, whose sequences incorporate that of the above nonamer and which can form "hairpin" duplices, are in progress. Intramolecular cyclization of the protected nonamer (**18**) is also under investigation.

Acknowledgment. This research was supported by the Medical Research Council of Canada (Grant MA 3428).

(11) B. F. C. Clark, S. K. Dube, and K. A. Marcker, *Nature (London)*, **219**, 484 (1968).

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2,3-Naphtho-2,5-bicyclo[2.2.0]hexadiene

Sir:

This communication deals with the chemistry of 2,3-naphtho-2,5-bicyclo[2.2.0]hexadiene (**1**). The fluorescence of **1** at room temperature is a superposition of emission from **1** and its photorearranged product, anthracene (Figure 1). This observation suggests that an appreciable amount of the anthracene formed in the photorearrangement is in the singlet excited state. The reaction thus provides the first example known to us of the rearrangement of one excited molecule to another, both being in their respective singlet excited states. Although there are known examples of photochemical formation of electronically excited products, most of these reactions involve fragmentation, ionization, or complex formation rather than rearrangement.[1] Turro, *et al.*, have reported the photorearrangement of naphthvalene to triplet naphthalene at 77°K, which illustrates the rearrangement of one excited molecule to another in a different spin state.[2] Based on the analysis of the behaviors of various transients formed during the nanosecond laser photolysis of triphenylamine or tetramethyldianthrone,[3,4] the rearrangement of one triplet state molecule to another has been suggested.

Compound **1** was synthesized by a scheme similar to that reported for benzobicyclo[2.2.0]hexadiene[5] and exhibits the following properties: mp (uncor) 67°, 208°; *Anal.* (found) C, 93.92 and H, 6.04; ir (KBr) 3100, 2950, 880, and 760 cm^{-1}; uv$_{max}$ (cyclohexane) 231 (60,700), 266 (5860), 275 (6280), 287 (4180), 307 (700), 316 (335), and 321 nm (921); nmr (CD_3CN) δ 4.61 (m, 2), 6.67 (m, 2), 7.41 (sextet, 2), 7.64 (s, 2), and 7.83 ppm (sextet, 2). The sextets at 7.41 and 7.83 δ are those of an A_2X_2 system, and the analysis indicates that $J_{1,2}$ = 8.0, $J_{1,3}$ = 2.0, and $J_{2,3}$ = 6.5 Hz.[6] No peaks attributable to anthracene were detected in the ir and nmr spectra; however, peaks at 253 (8170) and 338 nm (68) in the uv spectrum indicate the presence of about 1.5% of anthracene.

(1) A. Zweig, *Pure Appl. Chem.*, **33**, 406 (1973).
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(3) E. W. Förster and K. H. Grellman, *Chem. Phys. Lett.*, **14**, 536 (1972).
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(5) R. N. McDonald, R. G. Frickey, and G. M. Muschik, *J. Org. Chem.*, 37, 1304 (1972); R. N. McDonald and G. M. Muschik, *J. Amer. Chem. Soc.*, **90**, 5315 (1968).
(6) J. A. Pople, W. G. Schneider, and H. J. Bernstein, *Can. J. Chem.*, **97**, 2798 (1964).

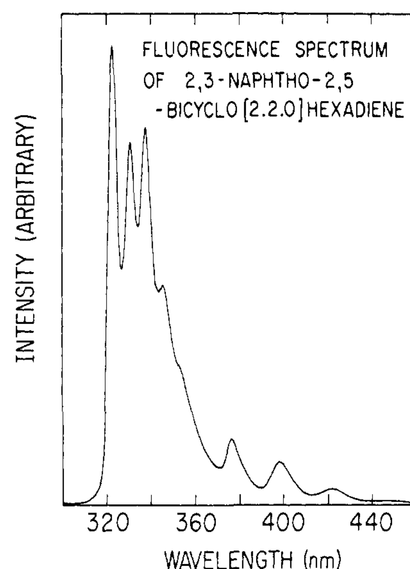
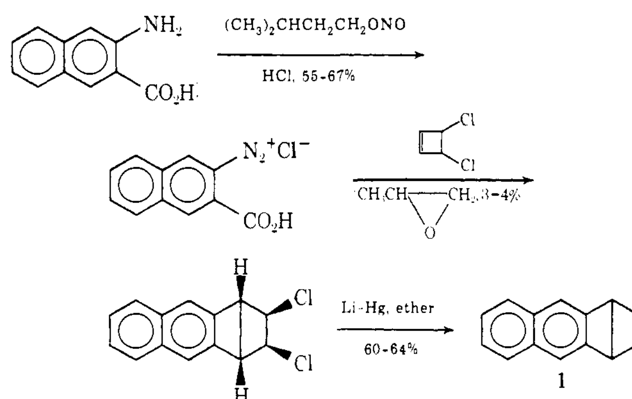


Figure 1.



Compound **1** decomposes thermally and photochemically (ϕ_{313nm} = 0.41 ± 0.02) to give anthracene quantitatively. From the rates of thermal decomposition in *n*-heptane between 36–60°, the activation energy was found to be 26.5 kcal. We were unable to detect chemiluminescence when **1** or a mixture of **1** and 9,10-dibromoanthracene was heated rapidly above 100°; *i.e.*, we were unable to detect the adiabatic formation of S_1 of anthracene by direct population, T–T annihilation, or energy transfer to dibromoanthracene.

The fluorescence spectrum of **1** (Figure 1, $\lambda_{excitation}$ 270–275 nm), which differs from those typical of naphthalenes, shows two progressions, a naphthalene-like emission beginning around 320 nm and the characteristic anthracene emission beginning around 370 nm. The uncorrected excitation spectra monitored at either 330 or 400 nm correspond, qualitatively, to the absorption spectrum of **1**. The emission spectrum from a nitrogen saturated solution does not vary appreciably with exciting light intensity at 270–275 nm nor with concentration ranging from 2.1 × 10^{-5} to 1.8 × 10^{-4} *M* (which contain about 3.6 × 10^{-7} to 3.1 × 10^{-6} *M* of anthracene, respectively). The lifetime of emission, measured by the time-controlled single photon counting technique at 330, 379, and 400 nm, was found to be 24.5 ± 0.3 nsec, compared to that of anthracene which is 4.9 nsec.[7] The possibility of the anthracene emission

(7) I. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965, p 123.