gold clusters up to Au_{11}.[7] One organocopper monomer has been reported.[8]

We wish to report the first examples of organocopper tetramers, pentafluorophenylcopper (**1**) and *o*-(trifluoromethyl)phenylcopper (**2**).

These were prepared from the corresponding aryl bromides *via* the Grignard in ether, metathesis with cuprous bromide, removal of magnesium bromide as its insoluble dioxane complex, isolation of the ether-soluble organocopper, and recrystallization from benzene.[9] These analyze well, have sharp infrared and ^{19}F nmr spectra that resemble those of other derivatives of pentafluorobenzene and *o*-benzotrifluorides, and like most organocoppers are easily oxidized by air and hydrolyze in water. All work was done in a nitrogen atmosphere.[10]

Compound **1**, which has been prepared by others in an impure state,[11] is a nearly white solid which melts and quickly decomposes at 210–220°, giving copper metal and decafluorobiphenyl. It is a mild Lewis acid, forming isolable complexes with σ bases such as dioxane, tri-*n*-butylamine, and benzonitrile, and π bases butyne-2 and 1,5-cyclooctadiene. **2** also is nearly white, decomposes at 200–205° giving 2,2′ bis(trifluoromethyl)biphenyl, and forms complexes less readily than **1**.

The aggregation of **1** in benzene was determined cryoscopically as 3.75–3.85, and by vapor pressure osmometry as 3.95. The mass spectrum of **1** was obtained by direct injection of a solid sample at 160–190° into a Consolidated Electrodynamics Corp. 21-110B high-resolution mass spectrometer at an ionizing voltage of 70 eV. The most abundant species other than decafluorobiphenyl is the parent ion for tetrameric **1**, *m/e* 920.[12] There were no fragments with more than four coppers. The relative abundances were *m/e* 920 (100), 753 (15), 690 (85), 523 (85), and 460 (40). Although significant quantities of trimer (*m/e* 690) and dimer (*m/e* 460) were detected, these much more volatile aggregates were less abundant[13] than tetramer. We consider that the mass spectrum is related to the composition of the solid, and that, taking into account volatility differences, the solid is almost all tetramer.[14]

The aggregation of **2** in benzene was found cryoscopically to be 3.82 and 4.28. The mass spectrum of **2** was obtained similarly at 130–190°. The relative abundance of *m/e* 832 (tetramer) was 100, 624 (trimer) and 416 (dimer) were both less than 1, and 208 (monomer) was less than 0.1. Surprisingly, a peak corresponding to $CF_3C_6H_4Cu_4F_2^+$ of *m/e* 435 was much more abundant (20) than monomer, dimer, and trimer. The tetramer **2** is very stable and much less contaminated by other oligomers than **1**. *Thus, the tetramers* **1** *and* **2** *are remarkably stable, not appreciably dissociating at 5° in benzene solution or at 190° under high vacuum in the mass spectrometer.*

We assume the tetramers have central copper tetrahedra as does $[CuS_2CN(C_2H_5)_2]_4$.[2d] Organolithiums likewise form tetramers[15] and $(CH_3Li)_4$ has a central Li_4 tetrahedron.[16] Organolithium clusters are quite thermally stable. The mass spectrum of ethyllithium has parent ions of $Et_5Li_6^+$ and $Et_3Li_4^+$ but no $Et_6Li_6^+$ or $Et_4Li_4^+$.[17] The aryl groups of **1** and **2** have ir and nmr spectra resembling those of normal covalently bound aryl groups even though they may be bridging copper atoms.

The ^{19}F nmr spectra of **1** and **2** vary with temperature. We feel that these changes may be due to changes in solvent complexes or rotamer populations.

Both **1** and **2** are much more thermally stable than the octameric meta isomer of **2** and undergo copper metal catalyzed decompositions without forming colored solutions. When **1** was decomposed in benzene with a copper catalyst, no $C_6F_5C_6H_5$ and thus no free C_6F_5 radicals were detected. On the other hand, the octamer decomposition is not copper catalyzed and forms a stable deep green R_6Cu_8 intermediate. The difference in stability of the organocopper clusters relative to size and structure is under study, and we are currently exploring cluster substitution reactions and ligand exchange upon mixing cluster compounds.

Acknowledgments. We gratefully acknowledge the work of Mrs. Flora C. Youngken and Mr. Fulton G. Kitson in obtaining molecular weights and mass spectra and Mr. Paul Davidson and Miss Joyce Dillard for assistance with the experimental investigations.

---

[7] M. McPartlin, R. Mason, and L. Malatesta, *Chem. Commun.*, 334 (1969).

[8] F. A. Cotton and J. Takats, *J. Amer. Chem. Soc.*, **92**, 2353 (1970).

[9] A. Cairncross and W. A. Sheppard, *ibid.*, **90**, 2186 (1968).

[10] We have stored samples for 5 years in a Dry Ice chest with no change. Under these conditions organocoppers show no tendency to carboxylate.

[11] (a) R. J. DePasquale and C. Tamborski, *J. Org. Chem.*, **34**, 1736 1969); (b) S. S. Dua, A. E. Jukes, and H. Gilman, *J. Organometal. Chem.*, **21**, 241 (1970), and references therein.

[12] Because of the ^{63}Cu, ^{65}Cu isotopes the pattern for the tetrameric species ranges from 920 to 928 in relative ratios expected from the isotopic abundances. Patterns corresponding to isotopic abundances are also found for other *m/e* positions.

[13] This crude approximation assuming equal ionization potentials for all aggregates undoubtedly is wrong. The conclusion that the less volatile tetramer is by far the most abundant species seems justified.

[14] Dimer and trimer might arise from dissociation of tetramer, but not the reverse. The spectrum does not change much with observation time. Interpretation is made difficult by continuous decomposition to decafluorobiphenyl. Some samples show peaks due to $(C_6F_5Cu)_4$-(C_6F_4). Occasionally the preparation of **1** goes awry, giving 3,4,5,6,-2′,3′,4′,5′,6′-nonafluorobiphenylcopper.

[15] L. D. McKeever and R. Waack, *Chem. Commun.*, 750 (1969).

[16] E. Weiss and G. Hencken, *J. Organometal. Chem.*, 21, 265 (1970).

[17] J. Berkowitz, D. A. Bafus, and T. L. Brown, *J. Phys. Chem.*, **65**, 1380 (1961).

Allan Cairncross,* Hisanori Omura, William A. Sheppard
Contribution No. 1740, Central Research Department
Experimental Station, E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

Received November 12, 1970

Studies in Linear Dichroism. V.[1] Spectroscopic and Conformational Properties of the Benzyloxy Group

Sir:

Previously we have described a method[2,3] which enables correlation of the values of dichroic ratios ($\mathbf{d}_0$) of compounds incorporated in stretched polyethylene films with the position of their chromophores relative to their longitudinal axis. This method is

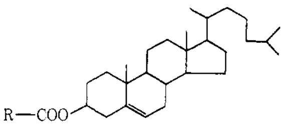
---

[1] Paper IV: A. Yogev, L. Margulies, and Y. Mazur, *Chem. Phys. Lett.*, in press.

[2] A. Yogev, L. Margulies, D. Amar, and Y. Mazur, *J. Amer. Chem. Soc.*, **91**, 4558 (1969).

[3] A. Yogev, J. Riboid, J. Marero, and Y. Mazur, *ibid.*, **91**, 4559 (1969).

Table I

	Band A			Band B			Band C[a]		
	λ, nm	d_0	α, deg	λ, nm	d_0	α, deg	λ, nm	d_0	α, deg
R = C_6H_5	197	1.6	45	230	5.5	13	295	4.3	21
R = o-$OCH_3C_6H_4$	204	1.9	41	235	3.0	30	293	1.8	42
R = o-$CH_3C_6H_4$	200	1.5	45	230	5.2	15	290	0.59	66
R = o-ClC_6H_4	203	1.8	42	233	2.9	31	284	<1.0[b]	>55
R = m-$OCH_3C_6H_4$		b		240	4.1	22	300	1.00	55
R = m-$CH_3C_6H_4$	202	1.8	42	233	5.7	12	290	0.50	69
R = m-ClC_6H_4	203	2.0	40	230	3.9	24	290	0.50	69
R = p-$OCH_3C_6H_4$[c]	200	2.0	40	255	6.6	0			
R = p-$CH_3C_6H_4$[d]	202	1.7	43	237	5.8	11	280	>1.0[b]	<55
R = p-ClC_6H_4[d]	202	1.6	45	240	5.2	15	280	2.0	40

[a] Estimated 0–0 band. [b] The concentration in the film was not appropriate for an accurate dichroic measurement. [c] This chromophore shows an additional band at 215 nm with $d_0 = 0.58$ ($\alpha = 66°$). Because of overlap with band A, this value may be actually smaller. [d] This chromophore shows an additional band at 210 nm with $d_0 < 1.0$. The overlap with band A impedes the dichroic ratio measurement.

Table II

	Band A			Band B			210–220-nm		
Compound	λ, nm	d_0	α, deg	λ, nm	d_0	α, deg	λ, nm	d_0	α, deg
p-$OCH_3C_6H_4COOH$	200	3.2	32	260	8.8	0	218	0.35[a]	74
p-$CH_3C_6H_4COOH$	202	1.2	46	243	8.1	8	210	0.68[a]	62
p-ClC_6H_4COOH	200	2.0	41	247	6.0	17	211	0.57[a]	65

[a] Because of overlap with band A this value may be actually smaller.

based on the use of[4]

$$d_0 = \frac{\epsilon_{\parallel}}{\epsilon_{\perp}} = \frac{f\cos^2\alpha + {}^1/_3(1-f)}{{}^1/_2 f\sin^2\alpha + {}^1/_3(1-f)} \qquad (1)$$

where f and α are the fraction of orientation and the angle between the transition moment of the chromophore and the longitudinal axis of the molecule, respectively.

This method was applied to compounds possessing α,β-unsaturated ketone function[3] within the skeleton of the incorporated material. Now we wish to report on the extension of our method to other chromophores located outside the molecular skeleton.

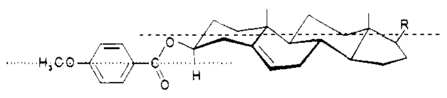
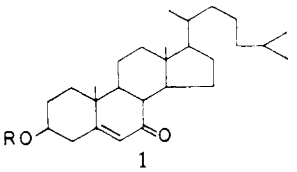


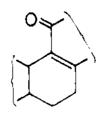
Figure 1. Conformation of the benzyloxy group in cholesteryl p-methoxybenzoates: (- - -) longitudinal axis of the molecule; (. . .) direction of the transition moment of the ET band.

We have measured the linear dichroic spectra of benzoic esters and monosubstituted benzoic esters of cholesterol incorporated in polyethylene films.[5] The resulting dichroic ratios (d_0) of the various bands of the benzoate chromophore are listed in Table I.

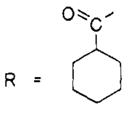
Since the molecular dimensions of all these esters are similar, we assume that their longitudinal axes, as well as their fractions of orientation, are the same. Further, it may be argued that substituting a benzyloxy by a cyclohexanoxy group in cholesterol will not change either property.[2] These assumptions permit the use of d_0 values of cyclohexanoxy α,β-unsaturated ketones **1** and **2** to evaluate f and to define the longitudinal axis



1



2



of the above-mentioned cholesteryl esters using the method described in previous publications.[2,3] The method consists of substitution of the d_0 values of **1** and **2** (1.8 and 0.35, respectively) separately into eq 1, which gives a set of two equations. The relative position of the transition moments of the two chromophores in **1** and **2** is such that the two angles they form with the longitudinal axis (α_1 and α_2) are interrelated by $\alpha_1 + \alpha_2 = 120°$.[3] Using this relation, the two equations were solved giving $f = 0.65$. The resultant position of the longitudinal axis is shown in Figure 1.

We have listed in Table I the α values for the bands of cholesteryl benzoate and monosubstituted benzoates which were calculated using eq 1 ($f = 0.65$). It may be seen from these data that the transition moment for the B band (ET band)[6] in cholesteryl p-methoxybenzoate is parallel to the longitudinal axis of the entire molecule ($\alpha = 0°$). In addition it may be assumed that this transition moment is in the plane of the chromophore. The rotational conformation of benzyloxy chromophore around the C_3–O bond which meets these requirements is the one in which the carbinyl hydrogen is eclipsed with the C=O bond (Figure 1). The transition moment of the ET band in this rotamer passes through

---

[4] Cf. M. Beer, *Proc. Roy. Soc., Ser. A*, **236**, 136 (1956).

[5] For description of the instrument, *cf.* J. H. Jaffé, H. Jaffé, and K. Rosenheck, *Rev. Sci. Instrum.*, **38**, 935 (1967).

[6] For spectroscopic definition of this band, *cf.* (a) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954); (b) S. Nagakura, *ibid.*, **23**, 1441 (1955); (c) J. Tanaka and S. Nagakura, *ibid.*, **24**, 1274 (1956); (d) J. Tanaka, S. Nagakura, and M. Kobayashi, *ibid.*, **24**, 311 (1956); (e) H. Harada and K. Nakanishi, *J. Amer. Chem. Soc.*, **90**, 7351 (1968).

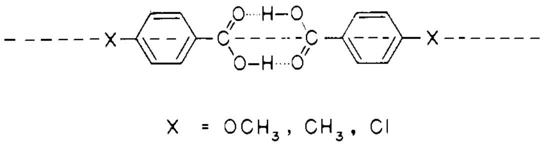


Figure 2. Para-substituted benzoic acids. (- - -) direction of the longitudinal axis and of the transition moment of the ET band.

the carbonyl carbon and the neighboring carbon atom as shown in Figure 1.[7]

We have corroborated the latter assignment using dichroic ratio values of three para-substituted benzoic acids (Table II). Previously we have shown that benzoic acids incorporated in stretched polyethylene films are completely dimeric. Using the same reasoning as previously, we deduce that the three acids have the same fractions of orientation and that their longitudinal axis is in the plane of the molecules (Figure 2). These assumptions allow the use of the differences in α values ($\Delta\alpha$) between two para-substituted esters for the corresponding acids. Solving eq 1 for the acids, using $\Delta\alpha$ values of the esters, gives $f = 0.72$. Since, as shown in the Tables I and II, the calculated α's of the corresponding acids and esters are identical within experimental error, the longitudinal axes in both series of compounds have the same relations to the benzyloxy chromophores. Thus all α values in Tables I and II define the angles which the transition moments form with the axis passing through the carbonyl carbon and the neighboring carbon atom. However, when a particular band is composed of transitions having different polarizations the α's define merely their vectorial resultants.

From the data in Tables I and II the following may be seen: the shortest wavelength transition (A band)[8] has, in all compounds studied, similar values of "longitudinal" polarization.[9] At longer wavelengths, the para-substituted esters and acids exhibit an additional band having a "transversal" polarization.[9] Since both these bands are not well resolved, the actual $\mathbf{d}_0$ values of these bands may have smaller and larger values, respectively. In addition, it is not improbable that in other benzoic acids and esters the additional band is hidden below the A band.

Contrary to the case for A band, the polarizations of the B and C bands depend on the substituents in the benzene ring and their relative positions. It is to be pointed that the direction of polarization of the C band changes with vibronic states of this transition.

The knowledge of the direction of the transition moments enables the establishment of the rotameric conformation of benzyloxy groups also in other positions of a molecule, provided its f value is known.[10]

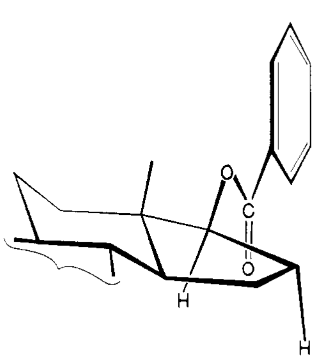
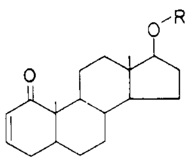
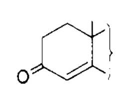


Figure 3. Conformation of the benzyloxy group in 17β-benzyloxyandrost-5-ene (only rings C and D are shown in the picture).

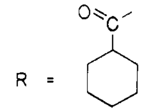
This may be exemplified by measurement of 17β-benzyloxyandrost-5-ene. We have established its fraction of orientation, f (0.37), by measurement of the $\mathbf{d}_0$ of 17β-cyclohexanoxy ketones **3** and **4** (1.64 and 2.14) and by substitution of these values into eq 1, remembering that $\alpha_3 + \alpha_4 = 60°$. This calculation gives us also the direction of the longitudinal axis of **3** and **4**. Assuming the same f and the same position of the longitudinal axis also in 17β-benzyloxyandrost-5-ene, and using the $\mathbf{d}_0$ value found for the B band of this compound (2.1), we have calculated the respective α.



3



4



Knowing independently the direction of the transition moment in the coordinates of the chromophore and the position of the longitudinal axis in the coordinates of the steroid skeleton, we have established the rotameric conformation of the benzyloxy substituent which is shown in Figure 3.

Similar treatment may be used to distinguish between axial and equatorial esters.

---

[7] In establishing this rotational conformation the values of the relevant bond angles were taken into consideration.

[8] (a) M. Ito, *J. Mol. Spectrosc.*, **4**, 144 (1960); (b) C. M. Moser and A. I. Kohlenberg, *J. Chem. Soc.*, 804 (1951); (c) H. E. Ungnade and R. W. Lamb, *J. Amer. Chem. Soc.*, **74**, 3789 (1952).

[9] Longitudinal and transversal polarizations are those which have dichroic ratios greater and smaller than 1.00, respectively.

[10] We have applied this method also to 3-benzyloxyandrostanes. In spite of a different fraction of orientation in these molecules, the same values of transition moments and of the conformation of the benzyloxy chromophore were obtained as in the analogous cholestane derivatives.

[11] C. P. Scott Research Fellow of the Weizmann Institute of Science.

[12] Predoctoral student of the Feinberg Graduate School.

* Address correspondence to this author.

Amnon Yogev,[11] Leon Margulies,[12] Yehuda Mazur*
Department of Chemistry
The Weizmann Institute of Science, Rehovot, Israel

Received September 16, 1970

The Alteration of Nuclear Magnetic Resonance Polarization in the Sensitized Photolysis of Benzoyl Peroxide[1]

Sir:

Nuclear magnetic resonance (nmr) emission and enhanced absorption were first reported 3 years ago. The polarizations could be produced in chemical reactions[2] as well as in photophysical processes.[3,4] In the much

---

[1] Presented in part at the 159th National Meeting of the American Chemical Society, Houston, Tex., Feb 1970, Abstract ORGN 42.

[2] (a) J. Bargon, H. Fischer, and U. Johnsen, *Z. Naturforsch. A*, **22**, 1551 (1967); (b) J. Bargon and H. Fischer, *ibid.*, *A*, **22**, 1556 (1967); (c) H. R. Ward and R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 1518 (1967); (d) R. Kaptein, *Chem. Phys. Lett.*, **2**, 261 (1968); (e) A. R. Lepley, *J. Amer. Chem.Soc.*, **90**, 2710 (1968).

[3] G. Maier, U. Haeberlen, H. C. Wolf, and K. H. Hausser, *Phys. Lett. A*, **25**, 384 (1967).

[4] M. Cocivera, *J. Amer. Chem. Soc.*, **90**, 3261 (1968). The irradia-