account the splitting between the ^{1}d–π^* and ^{3}d–π^* states, however, a somewhat larger gap and the opposite ordering are predicted. (A plausible singlet–triplet splitting is 1000 cm^{-1}, vide infra.) A similar calculation shows that the ^{3}d–π^* and $^{3}\pi$–π^* states have comparable energies in the dmp complex. Although these results are very approximate, they are consistent with the idea that the simultaneous emissions tend to arise from excited states with similar energies.

The remaining components that can be discussed are the extremely short-lived components ($\tau \lesssim 1$ ns) which have been resolved for the bpy and phen samples. As can be seen in Figure 7, in the case of the bpy complex this component gives a broad, structureless spectrum which is somewhat blue-shifted from the ^{3}d–π^* component. Similar behavior is observed for the phen complex.[12d] Due to their weak intensities, we do not have excitation spectra for these components, and therefore we cannot be as confident in assigning them to the respective $[Cu(biL)(PPh_3)_2]^+$ species or even in assigning them an orbital parentage. However, the most plausible assignments would be to CT states. The sub-nanosecond components occur at too low energies to be IL emissions from PPh_3,[40] and are probably too short lived to be MC emissions.[18] (We should note, however, that arguments based solely on lifetime date are somewhat tenuous.) In view of the relative energies and lifetimes of these components compared with those of the corresponding ^{3}d–π^* components, it is tempting to assign the sub-nanosecond components as ^{1}d–π^* emissions, but the results are too sketchy to do so at this time. It is curious in this regard that the sub-nanosecond components give spectra which are slightly broader than those of the ^{3}d–π^* components. Clearly the proper characterization of the sub-nanosecond components will require much further effort.

Conclusions

These studies illustrate the intriguing photochemical and photophysical properties exhibited by Cu(I) systems. In a general way the solution measurements involving $[Cu(dmp)(PPh_3)_2]^+$ demonstrate the need to define species in labile complexes of this type. The fact that PPh_3 dissociation appears only to be significant in the case of the dmp complex may be due to ligand/ligand repulsive effects associated with the methyl substituents in the 2 and 9 positions of dmp. Naively, one might have anticipated that the three, structurally analogous $[Cu(biL)(PPh_3)_2]^+$ complexes would behave very similarly, but our results show that the situation is much more subtle. The photoproperties are very sensitive to the nature of the biL ligand. Perhaps most striking is the fact that only the dmp complex gives rise to appreciable CT luminescence in solution at room temperature. An interesting challenge is to determine what interplay of steric, electronic, vibronic, etc., considerations is involved in determining the properties of photoexcited Cu(I) systems.

A final point worth noting is the possible connection between the Cu(I) systems that exhibit multiple emissions in a rigid glass and outer-sphere electron-transfer phenomena. The $[Cu(dmp)(PPh_3)_2]^+$ and $[Cu(phen)(PPh_3)_2]^+$ systems appear to exhibit ^{3}d–π^* and $^{3}\pi$–π^* emissions from geometrically distinct excited states, i.e., from separate minima in a configuration space. And the relatively slow interconversion between the states involved seems to depend on these states having similar energies. Formally, converting from the ^{3}d–π^* state to the $^{3}\pi$–π^* state can be viewed as a ligand-to-metal electron-transfer process, and conversely, converting from the $^{3}\pi$–π^* state to the ^{3}d–π^* state can be viewed as a metal-to-ligand electron-transfer process. Electron-transfer processes are known to be inhibited by the need for significant structural rearrangements in going from reactant to product states and, so long as the gap does not become too large, to occur more rapidly as the energy gap separating the reactant and product states increases.[41]

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Communications to the Editor

Circular Dichroism of (C_3)-Cyclotriveratrylene-d_9: An Example of Exciton Optical Activity due to Isotopic Substitution

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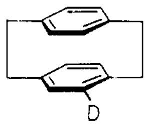
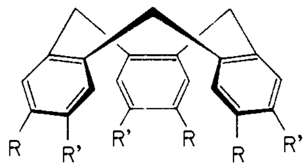
Recently, intense interest has been devoted to the study of the chiroptical properties of compounds owing their chirality to the presence of deuterium. In particular, the carbonyl chromophore has been extensively investigated.[1] In contrast, the only available example of an aromatic derivative showing relevant circular dichroism (CD) properties is (S)-(−)-4-deuterio[2.2]paracyclophane (**1**).[2]



S(−)·1



	R	R'
P(−)·2	OCH_3	OH
M(−)·3	OCH_3	OCD_3
P(−)·4	OC_2H_5	OCH_3
M(−)·5	OC_2H_5	O iC_3H_7
M(−)·6	OCH_3	O iC_3H_7

In a previous paper,[3] we reported the CD spectra of some (C_3) chiral derivatives of cyclotriveratrylene (CTV) and their interpretation in terms of exciton coupling between the transition

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(2) Hoffman, P. H.; Hong, E. C.; Weigang, O. E., Jr.; Nugent, M. J. *J. Am. Chem. Soc.* **1974**, *96*, 2620.

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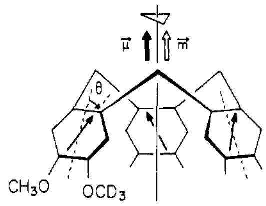

Figure 1. Symmetric coupling of the benzene B_{2u} electric transition moments in (*M*)-(−)-**3**, giving positive CD at high energy (and negative at low energy).

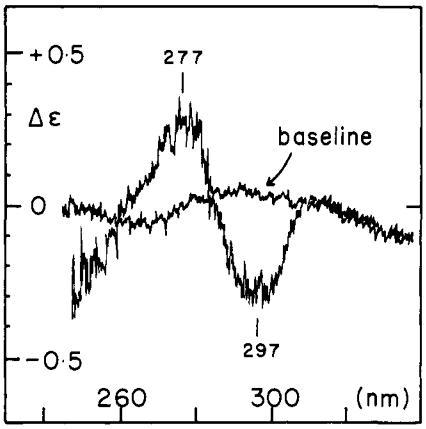

Figure 2. Circular dichroism spectrum[21,22] of (*M*)-(−)-**3**.

moments of the three aryl chromophores. The presence of substituents R and R′ having spectroscopic moments[4] of different magnitudes causes a rotation of the electric transition moments from the symmetrical positions (angle θ in Figure 1). As a consequence, it was suggested that the CD of these compounds would provide a sensitive differential measurement of the relative magnitudes of nearly identical spectroscopic moments. In fact, even a very small deviation of θ from zero originates intense exciton CD. Keeping this last point in mind, we thought this system would be sensitive enough to evidence isotope substitution effects.

In this communication, we report the CD spectrum of (C_3)-cyclotriveratrylene-d_9 (**3**), which shows a remarkably clear exciton couplet of considerable intensity[5] (Figure 2), corresponding to the B_{2u} benzene-like transition. The synthesis of this compound and the determination of its absolute configuration have been described separately.[6,7] In Table I are assembled the characteristics of the CD spectra of related C_3-CTV derivatives having different alkyl substituents, together with that of the parent triphenol **2** for comparison.[7-9]

In the light of the exciton interpretation previously proposed,[3,10] we can deduce from the experimental CD data the following sequence[11] of spectroscopic moments:

$$\mathrm{OH} > \mathrm{OCD_3} > \mathrm{OCH_3} > \mathrm{OC_2H_5} > \mathrm{O\text{-}}i\mathrm{\text{-}C_3H_7}$$

Table I. Circular Dichroism Spectra of (C_3)-Cyclotriveratrylene Derivatives[21,22]

	$[\alpha]_D$ ($CHCl_3$), deg	λ	Δε	B_{1u} λ	B_{1u} Δε	B_{2u} λ	B_{2u} Δε
(*P*)-(−)-**2**	−253	208	−47	236	+3.0	277	+3.8
				249	−11	299	−5.3
(*M*)-(−)-**3**	−3.2			250	(−)	277	+0.26
						297	−0.30
(*P*)-(−)-**4**	−20			233	−5.5	276	+3.0
				252	+4.1	296	−3.0
(*M*)-(−)-**5**	−47	213	−33	230	+4.5	276	−7.5
				248	+1.7	295	+5.2
(*M*)-(−)-**6**	−14	213	−21	232	+12.5	276	−9.5
				253	−5.0	295	+8.0

It is currently accepted that the spectroscopic moment of the methoxy group is connected with the resonance effect,[14] which is maximum when the methyl group lies in the plane of the benzene ring. With regard to this the drastic loss of intensity observed for the B_{2u} transition in 2,6-dimethylanisole[15] is certainly relevant. Other examples of loss of absorption intensity caused by inhibition of the resonance due to steric effects are numerous in the literature.

From a ^1H NMR study in liquid crystalline solution, Emsley et al.[16] have recently shown that in 2,6-dichloroanisole the C–O–C and the phenyl planes are orthogonal. More specifically, *o*-dimethoxybenzene in the gas phase and solution was shown to exist in nonplanar conformations.[17] On the other hand, the preferred crystal state conformation of methoxybenzene derivatives is planar.[17] Deuterium substitution in compounds equilibrating rapidly between equivalent structures can cause a significant deviation in their relative populations; usually, although one exception was reported,[18] the heavier isotope is found to occupy preferentially the position of higher strain[19,20] on account of its smaller effective size with respect to the lighter isotope.

In light of these facts, the greater magnitude of the spectroscopic moment of the OCD_3 with respect to the OCH_3 group can probably be interpreted as being due to the higher population of the planar conformation (sterically more hindered) for the group bearing the heavier isotope. The sequence of spectroscopic moments reported above for the *O*-alkyl groups, where the magnitude diminishes with increasing size, can be understood in the same way.

The CD of this system therefore seems to be caused by inequalities of the spectroscopic moments originated from conformational effects. Further investigations involving CTV-like molecules in which the R and R′ groups cannot give rise to such conformational changes are in progress.

Acknowledgment. G.G. thanks C.N.R. (Rome) for financial support.

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(5) The CD spectrum of the deuterioparacyclophane **1** clearly shows only a negative maximum about one order of magnitude smaller.[2]

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(8) Collet, A.; Jacques, J. *Tetrahedron Lett.* **1978**, 1265.

(9) All compounds have enantiomeric purities in the range 90–100%; the specification of absolute stereochemistry by means of the P and M descriptors is discussed in ref 7.

(10) The interpretation proposed by Weigang et al.[12] for the CD of the deuterioparacyclophane **1**, which is based on the vibronic rotation of the transition dipole of the aromatic ring bearing the deuterium atom as a result of the smaller vibrational amplitude of the C–D bond, does not seem to apply in our case as the OCD_3 group gives a dissignate effect from OC_2H_5 and O-*i*-C_3H_7. This is not surprising since the isotope is not directly bound to the benzene ring, and its effect on the geometry should be negligible.[13]

(11) This sequence is pertinent only for the B_{2u} transition. A more complete interpretation of the CD spectra of compounds **2**–**6** will be given in the full paper.

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(21) The CD spectra of (−)-**2** and (−)-**4**–**6** were recorded on a Jouan-Dichrograph II instrument in methanol solution, that of (−)-**3** on a Jouan Dichrograph III in dioxane solution. The chemical purity of **3** (in particular, with respect to possible optically active contaminants) was assessed by several methods including TLC (on silica gel and alumina), NMR, mass spectrometry, and microcalorimetry (dsc).[6]

(22) The CD spectrum of a sample of enantiomer (+)-**3** having $[\alpha]_D$ +3.0° was run independently on a Jasco J-500A spectropolarimeter, giving the following results (in dioxane): 276 nm, Δε −0.23; 297 nm, Δε +0.26.[6]