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Conformationally Controlled Intramolecular Charge Transfer Complexes

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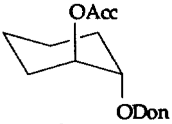
Summary: The formation of intramolecular charge transfer complexes between an electron-poor 3,5-dinitrobenzoyl fragment and electron-rich 4-substituted phenoxy fragments can be controlled by restricting the conformation of substituted cyclohexanes containing these fragments.

Intermolecular organic charge transfer (C-T) complexes arising from the interaction of π-electron donors and π-electron acceptors have been the subject of extensive experimental and theoretical study.[1] By contrast, there have been far fewer studies on the corresponding intramolecular C-T complexes.[2] In general, such studies have utilized compounds with donor and acceptor groups connected by flexible chains. We now wish to describe a system in which the C-T interaction is dependent upon the conformation of a cyclohexane ring, and in which the behavior of the two chair conformations can be directly compared.

1ee

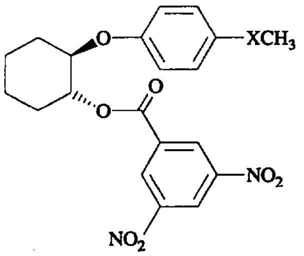


1aa

We sought to compare the behavior of *trans*-1,2-disubstituted cyclohexanes, in which the two substituents are free to adopt a diequatorial orientation, **1ee** with those in which the conformation is restricted to one with two axial substituents, **1aa**. The spectral behavior of the two systems would allow us to contrast a system in which the two substituents could approach each other and in which an *intramolecular* C-T interaction would be possible with one in which only *intermolecular* C-T interactions could occur.

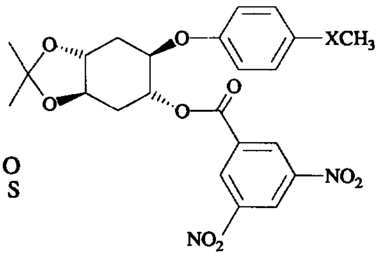
We reasoned that the energy of the C-T interaction would be sufficient to lock a conformationally flexible cyclohexane such as **2** into the **ee** conformation and constrained a comparison structure to the **aa** conformation by annulation of a *trans*-fused five membered ring as in **3**. Compounds **2** were readily prepared by treatment of cyclohexene oxide with the appropriate phenolate anion followed by esterification with 3,5-dinitrobenzoyl chloride. The rigid analog with diaxial substituents could be prepared in good yield from 1,4-cyclohexadiene.

The monoepoxide could be obtained by treatment of 1,4-cyclohexadiene with aqueous N-bromosuccinimide followed by sodium hydroxide[3]. Opening of the epoxide with concentrated potassium hydroxide was followed by *p*-toluenesulfonic acid catalyzed ketalization with 2,2-dimethoxypropane in dimethylformamide[4]. The intermediate conformationally locked olefin could be epoxidized, the oxirane opened with phenolate and esterification gave **3**. The epoxide opening is highly stereoselective, and only a single diastereomer of the protected ether alcohol could be detected[5].



2

a) R = O
b) R = S



3

Although an overlay of the electronic absorption spectra of **2b** and **3b** (shown in Figure 1) indicates an enhancement in the absorption of **2b** over **3b** near 400 nM, the absorption maximum is not readily visible. The presence of the C-T interaction is, however, immediately apparent in the difference spectra ([**2b**-**3b**], Figure 2). Both pairs of compounds (**2a**, **3a** and **2b**, **3b**) exhibit bands in the UV region which are extremely broad and tail into the visible region (**3a**-**2a** λ_{max} = 360 nM, $\varepsilon = 56$: **3b**-**2b** λ_{max} = 383 nM, $\varepsilon = 50$). It must be emphasized that although the values of ε are low, the bands are very broad, characteristic of charge transfer absorbtion bands, and the integrated intensities are quite high.

Fig. 1 Electronic Absorption Spectra for **2b** and **3b**

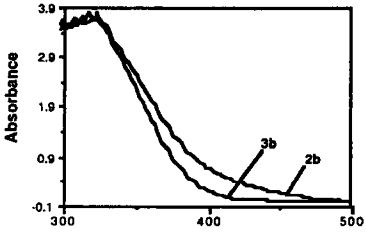
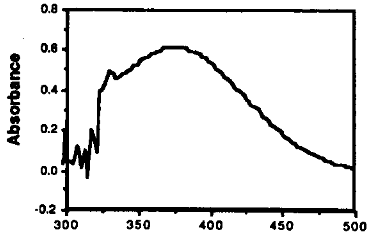
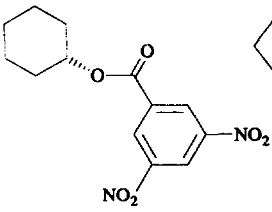
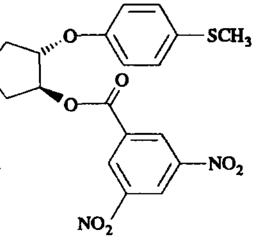


Fig. 2 Difference Spectrum [**2b** minus **3b**].

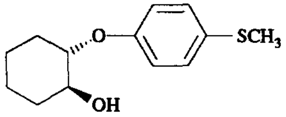




4



5



6

Although we regarded the locked diaxial ether ester **3** as the appropriate model to illustrate the conformational requirement for charge transfer complexation, we were able to measure the C-T bands in **2** using other models for subtraction. Since it is the dinitrobenzoate chromophore which makes the largest contribution to the long wavelength portion of the ultraviolet spectrum, we found that it was necessary to subtract the spectrum of this moiety, only. Thus the C-T bands can also be observed in difference spectra in which the spectrum of cyclohexyl 3,5-dinitrobenzoate, **4** is subtracted from the spectrum of **2**, although in this case the absorbtion maxima are slightly shifted.

The cyclopentyl analog **5** could also be used as a model for a system in which the electron rich and electron poor moieties are too far appart for effective charge transfer interaction. Difference spectra [**2b** - **5**] exhibited essentially the same charge transfer absorption, again with slight differences in the absorbtion maxima and extinction coefficients. Molecular modelling using the Macromodel program[6] illustrated the chromophoric similarity of the *trans* cyclopentane to **1aa** and its difference from **1ee**. We modelled the dimethoxy analogues of **2**, **3** and **5** and used the OCCO dihedral angles and O-O nonbonded distance as crude measures of the ability of the two substituents to approach each other. The dihedral angles do form a series in which the five membered ring compound is intermediate between the two six membered ring compounds (**2**;60°, **3**;177°, **5**; 133°). More significantly, the O-O distances fall into two categories; the two groups can approach closely in **2** but are held apart in **3** and **5** (**2**; 2.9Å, **3**; 3.7Å, **5**; 3.8Å).

We could form an intermolecular charge transfer complex analogous to the intramolecular complex in **2b** by taking a mixture of **4** and the ether alcohol **6** which was the precursor of **2b**. The position of the band was similar to that in the intramolecular complex but at slightly longer wavelength (λ_{max} = 396 nM in [(**4** + **6**) - **4**] as compared with λ_{max} = 376nM in **2b** - **4**.

Both the intramolecular complex in **2b** and the intermolecular complex in (**4** + **6**) were subjected to dilution studies to determine whether the Beer-Lambert Law was obeyed. The spectra of **2b** -**4** exhibited an unchanged extinction coefficient characteristic of an intramolecular complex upon one hundred fold dilution. By contrast, the spectra of (**4** + **6**) decayed rapidly upon twenty fold dilution as expected for an intermolecular complex.

Our results clearly indicate that the formation of intramolecular charge transfer complexes can be controlled by conformation and that the distance between the two linking oxygen atoms represents a critical parameter governing the possibility of significant intramolecular charge transfer interactions in our systems.

Footnotes and References

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