

STEREOCHEMISTRY OF OLEFINS—X OPTICALLY ACTIVE CHARGE-TRANSFER ABSORPTION OF π -MOLECULAR COMPLEXES

A. I. SCOTT* and A. D. WRIXTON†

Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut 06520

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Summary: The sign of the Cotton Effect has been related to the chirality of a series of π -molecular complexes of olefins with tetracyanoethylene (TCNE).

INTRODUCTION

THE GENERATION of new absorption bands on bringing together two organic compounds is well known.¹ Often these new absorption bands occur in the visible region giving rise to strong colors. The effect is generally attributed to a loose reversible association between the component molecules in a definite ratio (usually 1:1), permitting the transfer of an electron from one molecule to another.² Those molecules which tend to donate electrons are referred to as electron donors, D, and those which accept, as electron acceptors, A, and the process is facilitated by a low ionisation in D and a high electron affinity in A.

Mulliken² applied a simple quantum mechanical approach to such systems, assuming resonance between no-bond structures (A, D) and dative or charge transfer structures ($A^- - D^+$).



The ground state wave function ψ_N is then represented by,

$$\psi_N = a \psi_{D, A} + b \psi_{D^+, A^-}$$

where $a^2 \gg b^2$.

In the excited state, the wave function, ψ_E , is represented by,

$$\psi_E = a \psi_{D, A} + b \psi_{D^+, A^-}$$

where $a^2 \ll b^2$ (ie: the association is largely dative).

The transition from the ground state N to the excited state E is then equivalent to the transfer of an electron from the donor D to the acceptor A. Such a transition adequately accounts for the new absorption band observed and hence, the latter is referred to as the charge-transfer CT band.

Subsequently Orgel and Mulliken³ showed that charge transfer forces in the ground state were not a necessary criterion for the observation of a CT transition, and random encounters, under the influence of van der Waals forces only, could provide the necessary contact between donor and acceptor molecules (contact charge transfer). More recently⁴ no support for the dominant role of charge transfer contributions in the

* To whom all correspondence should be addressed.

† Present address: Institut de Chimie, Université de Strasbourg, Strasbourg, France.

ground state with such donor-acceptor systems could be obtained. In fact, loose association through van der Waals forces is consistent with the small heats of formation^{1b} of π -molecular complexes.*

With π -molecular complexes, the energy of the CT transition depends mainly on the difference between the ionization potential of the donor and the electron affinity of the acceptor.³ Thus, in general, the intermolecular CT band (N \rightarrow E) shifts to longer wavelengths for a lower ionization potential of the donor and a higher electron affinity of the acceptor. The intramolecular spectra² of the donor and acceptor are more or less modified by the association and may or may not contribute to the CT absorption where mixing is possible.⁵

It is probable that certain chemical reactions initially proceed through the association of reactants in a π -molecular complex before the formation of a σ -intermediate. The effect of such complexes would be to lower the activation barriers facilitating chemical reaction. Both Diels-Alder reactions and electrophilic substitutions of aromatic hydrocarbons or olefins are thought to involve π -molecular complex intermediates.^{1a, 6}

Structure

The observed properties of π -molecular complexes are statistical averages over all attainable configurations in thermal equilibrium. The most stable of these configurations (ie: that with lowest energy) is that in which maximum orbital overlap is obtained between donor and acceptor, and is modified by the steric requirements of each partner.⁵ With aromatic donors and acceptors, for example, maximum orbital overlap is attained when the planes of the two molecules lie parallel to each other, and this has been confirmed by X-ray work on solid π -molecular complexes.^{1a, 8}

The effect of steric requirements is shown with the complex formed between hexamethylbenzene and chloranil.^{1a, 9} Owing to the bulkiness of the Me and Cl substituents, the long axes of the two molecules are oriented by about 16° with respect to each other, even though their molecular planes remain approximately parallel. As a result, the aggregate becomes dissymmetric.

X-ray analysis¹⁰ of Br₂/C₆H₆ complexes has shown that the Br₂ molecule lies along the 6-fold axis of C₆H₆. Each Br atom is 3.36 Å from the nearest C₆H₆ molecule, and the Br-Br bond is little different from that in free-Br₂ molecules.

Optical activity in π -molecular complexes

Briegleb and Kuball¹¹ predicted that if either the donor or acceptor in π -molecular complexes is optically active, we may expect:

- (1) a change in partial rotational strength of a given absorption band which is responsible for the optical activity of the optically active component;
- (2) ORD and CD should be detectable within the range of the CT band;
- (3) any absorption band characteristic for the optically inactive component should exhibit CD as a result of loss of symmetry.

In fact,¹¹ ORD Cotton Effects were detected in the CT absorption region with optically active camphor and fenchone as donors with tetracyanoethylene (TCNE) as acceptor, and with optically active α -[2,4,5,7-tetranitrofluorenylideneaminoxy]-

* The term " π -molecular complex" is used with the same meaning as Dewar.*

propionate as acceptor with 2-methylnaphthalene, anthracene, stilbene and carbazole as donors. The observed effects were small owing to a predictably very small dissymmetry factor for charge-transfer processes, and, in the case of (+) 3-methyl cyclohexanone with TCNE as acceptor, no effect at all could be detected.

However, since Cotton Effects could be detected under CT absorption bands, and owing to the frequent occurrence of such CT bands in the visible or near UV, their possible application to dissymmetric olefins was examined.

π -Molecular complexes of olefins

Most studies¹ of π -molecular complexes have been concentrated upon those involving aromatic donors. This probably results from the fact that often such donors furnish complexes which are fairly readily isolated and characterized. However π -molecular complexes have been detected between olefins and tetranitromethane,^{12, 13} iodine,^{14–16} SO₂⁴² and TCNE.¹⁷

Tetranitromethane forms colored π -molecular complexes with olefins,¹² and the intensity of the absorption in the visible has been used as means of determining the degree of unsaturation of the double bond.¹³ The absorption was found to change with time,¹³ and recently,^{18, 19} it has been shown that certain nitro derivatives of olefins are readily formed under such conditions.

Iodine has also been used¹⁶ for a similar purpose in determining the degree of unsaturation of a double bond since the CT transition in the 300 nm region shifts to somewhat higher wavelengths on increased alkyl substitution. Like tetranitromethane, however, reaction is possible and photochemical addition of iodine to the double bond can readily occur.^{14, 16}

With SO₂⁴² olefins again give CT absorption in the 300 nm region, the position of which correlates with the ionisation potential of the hydrocarbon. Although reaction with olefins does not readily occur, SO₂ possesses the disadvantage of being a rather unpleasant smelling gas making operations with it less desirable.

The highly electronegative cyano groups so effectively withdraw electrons from the double bond of TCNE as to endow it with a very high electron affinity.^{20–23} It therefore can act as a very ready electron acceptor.^{22, 23} With condensed aromatic hydrocarbons it can form complexes stable enough in many cases to be isolated. With olefins,¹⁷ it exhibits CT transitions in the visible, the position of which changes markedly on progressive alkyl substitution of the olefin double bond. Apart from reaction with aromatic amino compounds,^{22, 24} ketones,²³ and Diels–Alder reaction with conjugated dienes,^{25, 26} the π -molecular complexes of TCNE, in general, do not possess the reactivity difficulties exhibited by tetranitromethane or iodine. For these reasons, it was considered to be the acceptor of choice.

RESULTS AND DISCUSSION

CH₂Cl₂ was used as the solvent for the study of the CT bands of π -molecular complexes of TCNE, since complexation is favored in chlorinated solvents and TCNE is reasonably soluble in this medium.²⁷ Solvents such as acetone, C₆H₆, EtOAc and EtOH, possess appreciable complexing affinity for TCNE and would, therefore, be unsuitable since competitive complexation processes would be set up. In order to show that the conditions used were of the same order of sensitivity to that used by

Briegleb and Kuball,¹¹ the CD spectra under the CT band exhibited by a number of ketones with TCNE were measured and are recorded in Table 1.

TABLE 1. CD SPECTRA (CT BAND) OF $\sim 10^{-1}$ M SOLUTIONS OF OPTICALLY ACTIVE KETONES IN TCNE SATURATED CH_2Cl_2 SOLUTION AT 25°; INSTRUMENT ANGLE SETTING 0.04, CELL PATH LENGTH 1 CM.

No.	Compound	Ellipticity	$\lambda_{\text{max}}^{\text{nm}}$	Sign of Ketone $n \rightarrow \pi^*$ Cotton effect
1	(+) Camphor	-1.25	390-400	+ ^a
2	(+) Fenchone	+ ^b		+ ^a
3	5 α -Cholestan-3-one	+0.27	~ 380	+

^a see A. Rassat in Chapter 16 of ref. 38

^b see ref. 11

The results for a number of optically active olefins with differing degrees of substitution are recorded in Table 2. Where CD bands were detected, the peak maxima were found to approximate to those of the visible CT absorptions. Like the electronic absorption spectra,^{17, 22} the CD bands were characteristically broad and featureless. Selected spectra are reproduced in Figs 1, 2.

TABLE 2. CD SPECTRA (CT BAND) OF $\sim 10^{-1}$ M SOLUTIONS OF OPTICALLY ACTIVE OLEFINS IN TCNE SATURATED CH_2Cl_2 SOLUTION AT 25°; INSTRUMENT ANGLE 0.04, CELL PATH LENGTH 1 CM

No	Compound	Predicted helicity	Ellipticity	$\lambda_{\text{max}}^{\text{nm}}$	Sign of Olefin $\pi \rightarrow \pi^*$ Cotton effects
4	(+) α -Pinene	+	+0.04	~ 530	+
5	(-) α -Pinene	-	-	~ 510	-
6	(-) β -Pinene	-	+0.49*	~ 470	+
7	(-) Limonene	-	-0.03	~ 500	-
8	3 β -Hydroxyergost-7,21-(22)-diene		-0.06	~ 520	
9	(-) <i>Trans</i> -cyclooctene	+	+0.11	~ 470	-
10	5 α -Cholest-2-ene	+	+0.02	~ 450	+
11	3-Methyl 5 α -cholest-2-ene	+	+0.01	~ 520	+
12	4,4-Dimethylcholest-2-ene	+	+0.023	~ 460	
13	Cholest-4-ene	+	+	~ 500	-
14	5 α -Cholest-6-ene 3 β -acetate	+	+	~ 460	
15	Cholesterol	-	-0.065	~ 460	+
16	Cholesteryl acetate	-	-0.05	~ 450	+
17	Dihydro-lanosteryl acetate			No detectable CD under CT band above 500 nm (negative CD band at ~ 315 nm)	
18	3 β -Acetoxyergost-8(14)-ene			No detectable CD under CT band above 500 nm (negative CD band at ~ 315 nm)	
19	3 β -Hydroxyergost-7-ene	-	-0.05	~ 500	-

* Measured after 1/2 hr from time of mixing

No effort has been made to calculate absolute ellipticity values, since only the sign of the CD band is of primary importance for our diagnostic purposes. Also, the application of the Benesi-Hildebrand²⁸ procedure for calculation of the required equilibrium constants has been shown^{3, 4} to lead to equivocal results, the equilibrium constants obtained depending on the wavelength positions used in their calculation.

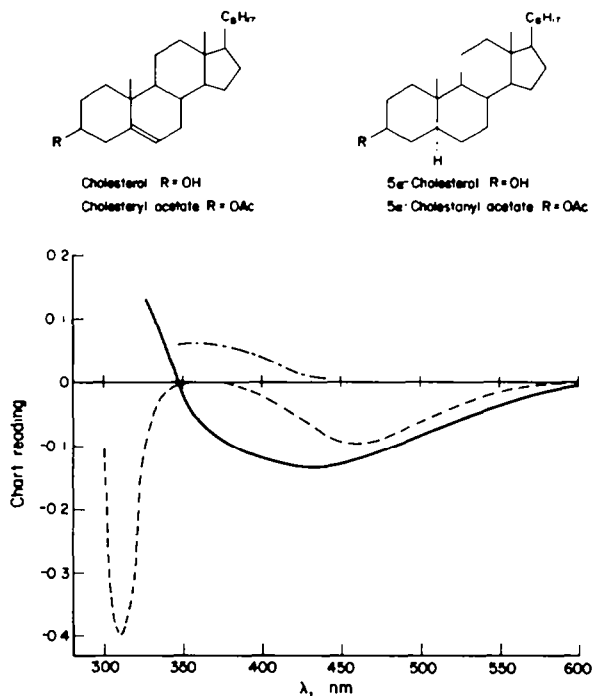


FIG. 1. CD spectra (angle setting 0.04, cell path length 1 cm) of: $\sim 10^{-1}$ M cholesterol (—), cholesteryl acetate (---), 5α-cholestanol (- · - · -), and 5α-cholestanyl acetate (·····) in TCNE saturated methylene chloride solution

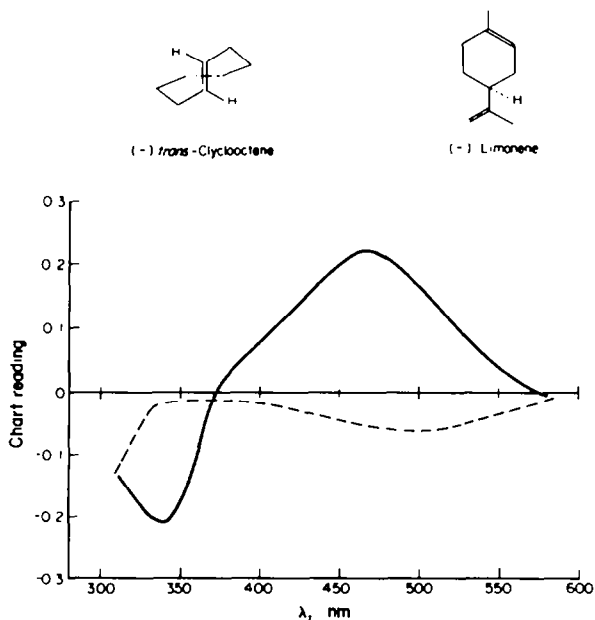


FIG. 2. CD spectra (angle setting 0.04, cell path length 2 cm) of $\sim 10^{-1}$ M (-) trans-cyclooctene (—) and (-) limonene (---) in TCNE saturated methylene chloride solution.

TABLE 3. CD SPECTRA (CT BAND) OF $\sim 10^{-1}$ M SOLUTIONS OF MISCELLANEOUS COMPOUNDS IN TCNE SATURATED CH_2Cl_2 SOLUTION AT 25° ; INSTRUMENT ANGLE SETTING 0.04, CELL PATH LENGTH 1 CM.

Compound	Ellipticity	λ_{max} , nm
5 α -Cholestanol	+0.03	~ 360
5 α -Cholestanyl acetate	-0.12	~ 325
(-)-Menthol	-0.042	~ 325
5 α -Cholestane	No detectable CD	
(+)-Cis-pinane	No detectable CD	

However, some qualitative comparison can be obtained from the ellipticities measured from the instrument, by using similar molar concentrations and conditions in each case. Such values would depend upon both equilibrium constants and absolute ellipticities.

Often additional lower wavelength optically active transitions were detectable, their presence sometimes being accounted for in terms of complexation with further functional groups present in the molecule. This was illustrated by the observation of optically active CT bands with menthol, 5 α -cholestanol and 5 α -cholestanyl acetate (Table 3 and Fig. 1). Where no other such functional groups were present, further CD bands (apart from those pertaining to the CT transition) may be ascribed to the complexed components,²⁹ shifted with respect to those of the uncomplexed

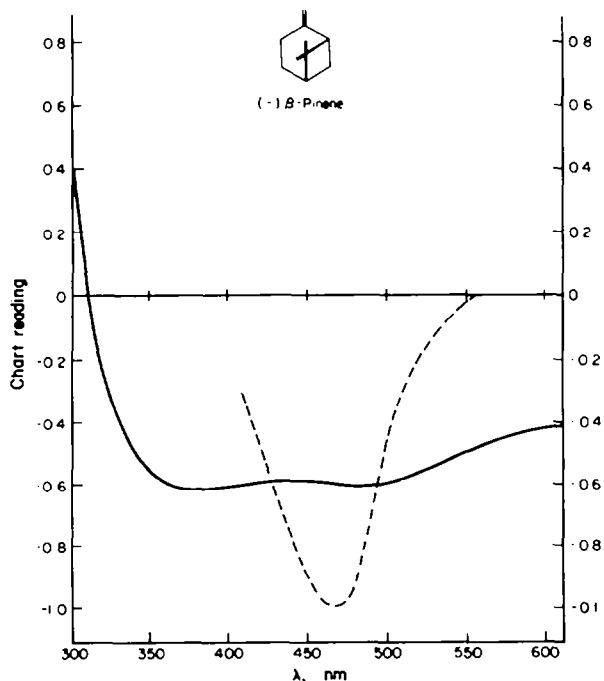


FIG. 3. ORD ——— (angle setting 0.1, cell path length 1 cm) and CD - - - - (angle setting 0.04, cell path length 2 cm) spectra of $\sim 10^{-1}$ M (-) β -pinene in TCNE saturated methylene chloride solution, measured after several hours.

components due to a mutual perturbation of the donor and acceptor energy levels³⁰ and the removal of restrictions on symmetry-forbidden transitions.³¹ The possibility that they arise from random contact charge transfer absorption with the saturated hydrocarbon residues of the optically active olefins seems unlikely, since so far, no CD spectrum has been detected for complexes of (+) *cis*-pinane or 5 α -cholestane with either TCNE or iodine as acceptor (Table 3). Contact CT absorption between such hydrocarbons is known to occur for both TCNE¹⁶ and iodine^{32, 33} with saturated hydrocarbons.

The spectrum obtained with (+) sabinene was somewhat inconclusive, even though definite CT bands were observed. Cyclopropane rings have been shown³⁴ to possess complexing affinity for such acceptors as iodine and it is probable that complexation with the cyclopropane ring of (+) sabinene is the complicating feature here.

Normally, equilibrium between donor and acceptor is reached very rapidly.^{1a} This has also been found to be the case here, since the ellipticity values did not appear to change with time. However (–) β -pinene represents a noteworthy exception. Both the visible absorption and the CD band increased with time, equilibrium being reached after several hours. The only other such case found in the literature³⁵ appears to be the complex formed between indene and methyl-4:6:4':6'-tetranitrodiphenate which interact at a measurable rate. However, in the latter case some doubt³⁶ exists as to whether the complex formed is a true π -molecular complex. With (–) β -pinene/TCNE, there is no reason to conclude that it is not a true π -molecular complex, since the position of the visible absorption band is normal¹⁷ for a disubstituted double bond and the color intensity, once at equilibrium, remained constant over a period of several weeks, after which time the olefin could readily be recovered unchanged. Reaction between the two species therefore does not seem possible and it is thought that the phenomenon may result from the steric requirements of the β -pinene molecule. It is interesting to note that the ellipticity value eventually reached for this compound with TCNE is the highest yet recorded for such olefin π -molecular complexes and that it is the only case where a noticeable change in the ORD during the course of determining the spectrum could be detected.

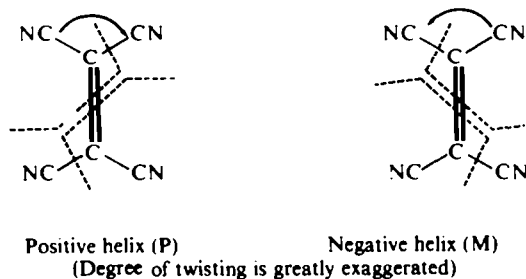
As expected for a fully conjugated π -electron system, TCNE is virtually planar.²² With polyaromatic systems, X-ray analysis in the crystalline state has shown⁸ TCNE to be plane parallel with the aromatic system allowing for maximum overlap. The molecules are found to be relatively far apart (~ 3 Å) accounting for negligible distortion of both donor and acceptor. Although no solid olefin/TCNE complex has yet been isolated, it is felt that the situation would be rather similar to the aromatic complexes so that maximum overlap is again achieved, taking account of the greater oscillation permitted in solution. Such oscillation will not have too much effect upon our arguments, since the observed properties depend on the average of the statistical distribution.

Unfortunately, as the dissymmetry factors for π -molecular complexes are small,¹¹ measurement of CD effects in the CT region requires the use of relatively large quantities of olefinic material. For this reason, insufficient experimental data is available for conclusive stereochemical correlations to be drawn. However, with the data at present available an apparent correlation between the sign of the olefin $\pi \rightarrow \pi^*$ Cotton Effects at about 200 nm, and the sign of the TCNE/CT CD band emerges. It is found (Table 2) that a reversal of sign between the $\pi \rightarrow \pi^*$ and CT

transitions is observed for the *trans*-olefins (–) *trans*-cyclooctene and 3 β -hydroxycholest-5-ene, whilst the *cis*-olefins 5 α -cholest-2-ene and (+) α -pinene retain the same sign for the original and CT transitions.

Alternatively it might be argued that the sign of the CT band bears no direct relationship to the olefin $\pi \rightarrow \pi^*$ transition. Although the olefin and TCNE probably have their C=C double bonds approximately parallel allowing for maximum overlap,⁷ and are relatively well separated, steric effects are bound to assume some importance.⁵ This has been shown with, for example, hexamethyl and hexaethyl benzene with TCNE,^{1*} the former aromatic hydrocarbon forming much more stable complexes than the latter. Steric requirements also permit an optically active acceptor to distinguish between the enantiomorphs of a racemic donor, a property used in the resolution of hexahelicene.³⁷ If steric effects are important here, we would expect the following consequences: (1) complexation will be favored on the less hindered side of the olefinic double bond as with complexes of platinum, and (2) some deviation from the totally parallel arrangement will occur due to the influence of adjacent substituents.

The CT absorption band is analogous to an intramolecular $\pi \rightarrow \pi^*$ band.⁵ With twisted chromophores the $\pi \rightarrow \pi^*$ band reflects the chirality or handedness of the twist and to a much lesser extent the vicinal effects from neighboring asymmetric carbons.³⁸ Since the application of a regional symmetry rule such as the octant rule for ketones³⁸ or that developed for platinum II complexes is found to be totally inappropriate, a plausible correlation for intermolecular CT processes could be derived from chirality effects. From a study of molecular models, invoking the importance of steric influences, such chirality effects appear to fit the observed Cotton Effect signs (Table 2). In this way, a positive CT band is associated with a positive helical array (P) and a negative band with a negative helical array (M).^{39, 41}



Most of the olefins studied possess one face which is much less hindered than the other, leaving little doubt regarding which side would be favored for complex formation. With the trisubstituted double bond of (–) limonene, either side appears to be about equally favored. However, models show that either side would produce the same sense of twist determined by the ring hydrogens.

The predicted helicity signs in Table 2 are derived for each olefin by aligning the appropriate Dreiding model with the TCNE model so that axially oriented allylic substituents are skewed in either the positive or negative helical array to minimize

steric overlap with the TCNE which in turn is introduced on the less hindered face of the olefin. In this way there is an overall agreement between the predicted and observed signs of the CT Cotton Effect for those olefins which display the phenomenon. Dihydrolanosteryl acetate and 3 β -acetoxyergost-8(:14)-ene (no 18) were the only olefins studied which did not produce CT absorption.

Further verification of the applicability of the above concept is in progress, but it is clear that the sign of the optically active CT transition yields information relating to the absolute stereochemistry of an olefin.

Although work, for the reasons already stated, has been concentrated on the complexes with TCNE, a cursory glance at the optical activity of iodine and tetranitromethane complexes with olefins, showed again that the CT bands possessed rotational strength (Table 4). There is, however, no reason to suggest that the rules for these

TABLE 4. CD SPECTRA (CT BAND) OF $\sim 10^{-3}$ M SOLUTIONS OF OPTICALLY ACTIVE OLEFINS WITH IODINE AND TETRANITROMETHANE AS ACCEPTORS

Compound	Sign with iodine	$\lambda_{\max}^{\text{nm}}$	Sign with tetranitromethane
5 α -Cholest-2-ene	-*	305-310	-*
(-) β -Pinene	+*	~ 300	+*

* No detectable CD under the visible absorption band of iodine

† CD in visible region, but no maximum reached.

complexes will be the same as for those with TCNE, since the orientation of the donor and acceptor in the complex in each case will vary with acceptor. With iodine, for example, by analogy with halogen-benzene complexes,¹⁰ it is probable that the iodine will be perpendicular to the olefin π bond.

One outstanding advantage of the π -molecular complex method if proved successful in absolute stereochemical work, is that the olefin is relatively unaffected in geometry by the presence of the acceptor and usually, after spectral measurement, the olefin can be quantitatively recovered. The latter can be accomplished by either the removal of TCNE with 1,3-butadiene, which rapidly forms a Diels-Alder adduct²⁵ which can be removed by fractional crystallization or chromatography, or chromatography on alumina, for which TCNE has a ready affinity forming a colored complex (this has previously been used for the separation of anthracene from a mixture with 2,4,7-trinitrofluorenone.⁴⁰

EXPERIMENTAL

For general conditions for obtaining spectra, source and purification of the olefins used, see ref. 43.

TCNE (Aldrich) was purified by sublimation at 50° under 0.1 mm pressure. Further purification could be achieved by recrystallization from chlorobenzene. CH_2Cl_2 was saturated with TCNE by shaking together for several hours. This solution was then filtered onto the given olefin until it was approximately 0.1 M in olefin. The CD spectrum was determined directly after mixing.

The olefin was most successfully recovered by chromatography on neutral alumina (Grade I). Generally, elution with pentane or pentane/ether gave good recovery of the olefin leaving the TCNE complexed to the alumina. Recovery of the olefin was also achieved by bubbling butadiene through the solution at 0°. Competitive π -molecular complex interactions were set up and rapid Diels-Alder addition of TCNE to butadiene gradually destroyed the olefin complex. Chromatography of the resulting mixture gave a ready separation.

Iodine and tetranitromethane complexes were prepared according to the literature procedures.^{13, 15}

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