10 were measured on a Hilger-Watts four-circle diffractometer (θ–2θ scans, Ni-filtered Cu Kα radiation, pulse height discrimination). The data for **2** were corrected for absorption, but the data for **10** were not. Both structures were solved by a multiple solution procedure.[7] All refinements were carried out by full-matrix least square (FMLS). The unweighted discrepancy index is given by $R = \Sigma||F_0| - |F_c|/\Sigma|F_0|$ and the weighted index by $R_w = [\Sigma w||F_0| - |F_c|^2/\Sigma w|F_0|^2]^{1/2}$.

Crystal data for **2** ($C_{22}H_{21}NO_4 \cdot \frac{1}{2}CH_2Cl_2$) follow: monoclinic, space group $C2/c$ or Cc, $a = 14.262$ (8), $b = 11.305$ (6), $c = 25.813$ (15) Å, $\beta = 99.80$ (4)°, $d_{obsd} = 1.31$ (2), $d_{calcd} = 1.314$ g cm^{-3} for $Z = 8$, μ (Cu Kα) = 18.9 cm^{-1}. Of 3884 accessible reflections with $\theta < 70°$, 2238 had intensities significantly greater than background [$I > 2.5\ \sigma\ (I)$]. The structure was obtained while working in the centrosymmetric space group $C2/c$. In the process of solving the structure, it was found that the crystal contains two different conformers of **2** which differ significantly only in the conformation of the heterocyclic six-membered ring. The presence of two conformers suggested the possibility that the space group was actually the noncentrosymmetric one, Cc. Since this space group has only four symmetry operations, the unique part of the unit cell would contain two independent molecules whose conformations need not be the same. The attempt to distinguish between $C2/c$ and Cc is described below.

The initial refinement of the structure was done in space group $C2/c$. The five carbon atoms of the heterocyclic six-membered ring were resolved into two sets of half-atoms corresponding to the two conformations of this ring. It was assumed that there are equal numbers of the two conformers in the crystal and that the two conformers are randomly distributed throughout the crystal, thus giving rise to a disordered structure. Isotropic temperature factors were used for the first few cycles of FMLS which were followed by several cycles of FMLS in which all atoms had anisotropic thermal parameters.

At this point the space group Cc was considered. There are two possible arrangements in Cc: (1) one independent molecule has conformation A and the other independent molecule has conformation B, and (2) vice versa. Refinements (isotropic temperature factors) of both arrangements were carried out. Both showed modest decreases in their R indices (R, R_w = 0.175, 0.228 and 0.174, 0.226 for the two trial structures in Cc) as compared to the corresponding values for the $C2/c$ refinement (R, R_w = 0.176, 0.240). Some decrease is expected because the number of independent variables is nearly doubled in Cc. Further refinement of these trial structures in space group Cc was not done because the reductions in the R values did not appear to be significant, particularly since both models showed almost equal decreases. Furthermore, the disordered model in $C2/c$ is more than adequate to establish the chemical structure.

The final refinement of the structure was carried out on the disordered model in space group $C2/c$. A difference Fourier calculated at the end of the anisotropic refinement showed peaks at reasonable positions for almost all the hydrogen atoms including those for the half-atoms. The idealized positions for all the hydrogen atoms were calculated and the hydrogen atoms were included in all subsequent calculations. In the final refinement, the hydrogen atoms were included in the structure factor calculations but their parameters were not refined. The final discrepancy index is $R = 0.099$ for the 2238 observed reflections. The final difference Fourier has only three features greater than 0.2 e Å^{-3} in magnitude. These are three peaks of about 0.5 e Å^{-3} which are located at 0.5–0.8 Å from the Cl atom of the solvent molecule. Stereodrawings of the two conformers of **2** are shown in Figure 1.

Crystal data for **10** ($C_{21}H_{22}N_2O_3$) follow: monoclinic, space group $P2_1/c$, $a = 10.901$ (5), $b = 12.230$ (5), $c = 14.769$ (12) Å, $\beta = 112.09$ (5)°, $d_{calcd} = 1.275$ g cm^{-3} for $Z = 4$, μ (Cu Kα) = 7.03 cm^{-1}. Of the 3716 accessible reflections with $\theta < 76°$, 2187 were considered observed [$I > 2.5\sigma\ (I)$]. The structure was solved by a multiple solution procedure as implemented in the computer program MULTAN.[8] The structure was not found on any E map calculated from phase sets based on an expansion of eight reflections (three origin defining reflections and five reflections of unknown phases). The number of starting reflections was increased to 11 and the resulting 256 phase sets were generated. An E map calculated from the phase set with the highest absolute figure of merit (FOM = 1.132, Karle R factor 30.8%) revealed all atoms except the hydrogens. The hydrogen atoms were located from a difference Fourier calculated after refinement of the heavier atoms. For the final refinement, anisotropic thermal parameters were used for the heavier atoms and isotropic temperature factors were used for the hydrogens; the hydrogen atom parameters were refined. The final R is 0.050 for the 2187 observed reflections. There are no features on the final difference Fourier of intensity greater than ±0.1 e Å^{-3}.

Registry No.—**1,** 57109-19-0; **2,** 57109-20-3; **3,** 38183-12-9; **8,** 36777-62-5; **10,** 57109-21-4; **11,** 57109-22-5; *o*-(α-hydroxycinnamoyl)benzoic acid, 43053-07-2; *N,N*-dimethylformamide dimethyl acetal, 4637-24-5; tripiperidinomethane, 22630-08-6; piperidine, 110-89-4.

Supplementary Material Available. Tables of the positional and thermal parameters for the structures of **2** and **10** (5 pages) will appear following these pages in the microfilm edition of this volume of the journal.

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Substituent Effects on the Electronic Nature of Carbon-Bonded Fluorine[1]

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We recently reported the surprising observation that certain lanthanide β-diketonates induce substantial shifts in the ^1H NMR spectrum of simple alkyl fluorides.[2] Here we wish to present results relevant to the nature of this interaction and describe its use to probe the electronic nature of organic fluorides.

Table I lists the magnitudes of selected ^1H and ^{19}F chemical shift, line width, and coupling constant differences induced by the addition of Yb(fod)$_3$ to a variety of alkyl fluorides. An examination of these results reveals that only relatively minor changes occur in the magnitude of the induced chemical shifts and spectral line widths as the steric bulk of adjacent centers is increased. Thus, steric factors do not have an overwhelming influence in determining the extent of substrate–lanthanide interaction. It is apparent, however, that the introduction of a second electronegative atom at the carbon bearing the fluorine atom produces a very significant *decrease* in both the induced chemical shifts and line widths while addition of Yb(fod)$_3$ has essentially no effect on the ^1H or ^{19}F spectra of compounds that contain two additional electronegative atoms at the fluorine-bearing carbon. Taken together, these results militate against a lanthanide–substrate interaction resulting from a principally electrostatic interaction between the electropositive lanthanide center and the electronegative end of the substrate molecular dipole since such an interaction, in contrast to what is observed, would be expected to increase as the resultant dipole moment of the substrate increases.

Table I
Influence of $Yb(fod)_3$ on Selected Values of the ^1H and ^{19}F Chemical Shifts, Line Widths, and Coupling Constants of Some Substituted Alkyl Fluorides[a]

Registry no.	Compd	^1H				^{19}F	
		$\Delta\delta_{CHF}$[b]	$\Delta\delta_{CH_3CF}$[b]	$\Delta W_{1/2}$[c]	ΔJ_{HCF}	$\Delta\delta$[d]	$\Delta W_{1/2}$
463-11-6	n-$C_8H_{17}F$	18.1		28.4	e	82	330
407-95-4	sec-$C_8H_{17}F$	10.0	11.4	25.0	e	99	400
75-10-5	CH_2F_2	0.49		9.0	0.0	1.6	<5
593-70-4	CH_2ClF	0.30		2.0	0.0	1.5	<5
75-45-6	$CHClF_2$	<0.01		<1.0	0.0	1.6	<5
75-43-4	$CHCl_2F$	<0.01		<1.0	0.0	0.3	<5
75-46-7	CHF_3	<0.01		<1.0	0.0	0.2	<5

[a] All chemical shift differences are reported in parts per million (ppm). Line widths and coupling constants are given in hertz. $[R-F] = 0.2-0.3\ M$, $[Yb(fod)_3] = 0.3-0.5\ M$ in CCl_4 solution. [b] ^1H chemical shifts are reported relative to internal tetramethylsilane recorded at 100 MHz. [c] Unless otherwise indicated, these values refer to resonances corresponding to hydrogens on the fluorine-bearing carbon. [d] ^{19}F chemical shifts are relative to internal CCl_3F, recorded at 94.1 MHz. [e] Accurate coupling constants could not be determined because of extensive broadening in the presence of $Yb(fod)_3$.

Several additional observations pertinent to the nature of the interaction between alkyl fluorides and $Yb(fod)_3$ are noteworthy. First, the broad, featureless ^{19}F NMR spectrum of $Yb(fod)_3$ becomes significantly more detailed upon the addition of an alkyl fluoride. Similar effects, purportedly a consequence of substrate–lanthanide association, are observed when other heteroatom-containing substrates are added to either $Eu(fod)_3$ or $Yb(fod)_3$.[3] Second, numerous attempts to obtain the ^1H and ^{19}F spectra of *tert*-butyl fluoride were thwarted by the rapid, $Yb(fod)_3$-induced polymerization of this substance.[4] This same reagent also induced the decomposition of both *exo*-2-fluoronorborane and benzyl fluoride, although reaction in these instances was noticeably slower than that observed for *tert*-butyl fluoride.[5] Finally, GLC analysis of the reaction mixture produced by the addition of $Yb(fod)_3$ (1.12 g, 1.06 mmol) to a solution of *tert*-butyl fluoride (0.659 g, 8.55 mmol) in CCl_4 (3.8 ml) indicated a substantial yield (~57%, based on *tert*-butyl fluoride) of an unspecified olefinic hydrocarbon(s) (mol wt 168.185; calcd for $C_{12}H_{24}$, 168.188),[6] which presumably arises from the trimerization of the isobutylene produced by the decomposition of *tert*-butyl fluoride.[7]

These observations indicate that the structure of the alkyl groups bonded to the fluorine exerts an influence on the relative stability of the alkyl fluoride in the presence of $Yb(fod)_3$ which is consistent with a decomposition pathway involving a Lewis acid assisted ionization of the C–F bond. This conclusion further supports the suggestion that the mechanism of substrate–lanthanide interaction involves, at least in part, the coordination of a covalently bonded fluorine atom to an ytterbium center in a manner similar to and accompanied by basically the same magnetic interactions associated with related phenomena witnessed for organic substrates containing other heteroatom centers. Moreover, it is apparent that the effect which progressive substitution of electronegative α substituents has on substrate–lanthanide interaction parallels the progressive decrease in bond length and the corresponding increase in the degree of ionic character of the C–F bond in such systems.[8]

These results suggest that certain lanthanide shift reagents can provide a sensitive probe with which to examine the electronic nature of covalently bonded fluorine atoms. An illustration of this application is seen in the influence of $Yb(fod)_3$ on the ^1H NMR spectra of benzyl fluoride and fluorobenzene. While the spectrum of benzyl fluoride exhibits a typical pattern of well-separated ortho, meta, and para hydrogen resonances,[9] that of fluorobenzene shows only a reduction of spectral resolution, unaccompanied by any significant separation of resonances. The differences in chemical shifts observed for these two substrates are presumably a reflection of the differing equilibrium constants which govern complex formation between substrate and lanthanide reagent. It follows that benzyl fluoride complexes more strongly with $Yb(fod)_3$ than fluorobenzene does. In light of the relatively minor role which steric factors play in determining the magnitude of the chemical shifts induced by $Yb(fod)_3$ in simple fluorocarbons, it further follows that these observed differences arise principally from the differences between the electronic character of the two fluorine centers.[10]

Experimental Section[11]

***n*-Fluorooctane** was obtained from Pierce Chemical Co. **Difluoromethane, difluorochloromethane, dichlorofluoromethane, trifluoromethane, fluorobenzene,** and **benzyl fluoride** were obtained as commercial samples from PCR. Inc. **Chlorofluoromethane** (Freon 31) was purchased from E. I. du Pont de Nemours and Co. The shift reagent $Yb(fod)_3$ was purchased from Willowbrook Laboratories and stored over phosphorus pentoxide. ***sec*-Fluorooctane**[12] and ***exo*-2-fluoronorbornane**[13] were prepared by literature procedures. ***tert*-Butyl fluoride** was obtained from Cationics, Inc.

Preparation of Samples. All reagents and solvents including internal standards were stored over molecular sieves (5A) which had been activated at 250° at 0.1 Torr for at least 24 hr. This procedure greatly reduced but did not completely eliminate the extraneous water signal observed in certain samples. Control experiments established that a significant portion of this extraneous water originated in the shift reagent, which was very difficult to dry completely. Samples were prepared in a glove bag using documented techniques.[14]

Acknowledgment. The authors are indebted to Dr. Dorothy Z. Denney for assistance in obtaining ^{19}F NMR data.

Registry No.—$Yb(fod)_3$, 18323-96-1; fluorobenzene, 462-06-6; benzyl fluoride, 350-50-5; *exo*-2-fluoronorbornane, 765-92-4; *tert*-butyl fluoride, 353-61-7.

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(4) In the absence of $Yb(fod)_3$, solutions of *tert*-butyl fluoride in CCl_4 showed no evidence of polymerization after several days.

(5) ^1H NMR analysis indicated that both substances (~0.3 *M* in CCl_4) were >50% decomposed after 1 hr in the presence of $Yb(fod)_3$ (~0.5 *M*). Under similar conditions, the spectra of 1- and 2-fluorooctane remained unchanged.

(6) Ir 1628 (m, C=C), 904 (m), 895 cm^{-1} (s, C=CH); ^1H NMR δ (CCl_4, relative to Me_4Si) 5.00 (s), 5.31 (s) (C=CH). No other volatile hydrocarbons were observed.

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(9) A similar spectrum was observed for benzyl alcohol in the presence of Yb(fod)$_3$.
(10) This observation is also consistent with, but does not require, the proposal of fluorine lone pair participation in p → p$_\pi$ back bonding in fluorobenzene. For a summary of the supporting and conflicting evidence regarding this proposal as well as a list of leading references, see ref 8.
(11) Infrared spectra were determined within sodium chloride cells on a Perkin-Elmer Model 225 grating spectrophotometer. NMR (^{1}H and ^{19}F) spectra were determined with a JEOL and Varian NMR spectrometers at 100 and 94.1 MHz, respectively. ^{1}H chemical shifts are reported in parts per million relative to internal tetramethylsilane. The internal standard for ^{19}F chemical shifts is as noted. All coupling constants are in hertz. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-7E mass spectrometer. Samples for spectral analyses were purified on a Hewlett-Packard Model 700 thermal conductivity gas chromatograph. Analytical GLC analyses were performed on a Hewlett-Packard Model 5750 flame ionization instrument. Absolute yields of products were calculated from peak areas using internal standard techniques.
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Secondary Orbital Effects vs. Steric Effects in Some Diels–Alder Additions

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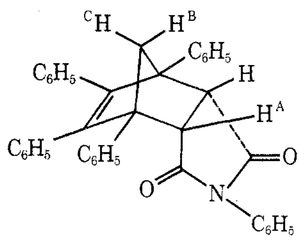
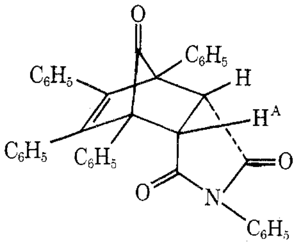
It has been found by several groups of workers that Diels–Alder addition of *N*-phenylmaleimide to heterocyclic dienes leads to formation of exo adducts.[1–4] The usual adduct, the endo isomer,[5] is not produced because either the nonbonded electrons on the heteroatom allow adequate overlap with the π electrons of the dienophile (*N*-phenylmaleimide) to produce the exo adduct or there is sufficient steric blocking to prevent formation of the endo adduct. The purpose of the study described below is to determine whether the possibility of exo-adduct formation results simply from steric hindrance or if the electronic interaction with π electrons of a bridged carbonyl group is operative.

We have determined the structures of endo adducts of *N*-phenylmaleimide to 1,2,3,4-tetraphenylcyclopentadiene (I) and 2,3,4,5-tetraphenylcyclopentadienone (II) which were isolated after 48 hr of reflux in xylene.



I
mp 241°



II
mp 226°

H_A (2 H, δ 4.26, singlet)
H_B (1 H, δ 2.36, doublet, $J = 9$ Hz)
H_C (1 H, δ 3.21, doublet, $J = 9$ Hz)

H_A (2 H, δ 4.28, singlet)

Several groups of workers have shown a four-bond spin–spin splitting coupling constant of approximately 3 Hz for the protons at the extremities of the fixed W formation in bicyclo[2.2.1]heptane systems;[6,7] specifically, the anti proton in the methylene bridge and the endo protons in the ethylene bridge show mutual splitting. The absence of coupling of H_A and H_C in I suggests the endo structure of the adduct.

The structure of II was shown by Eu(fod)$_3$-d_{27}–CDCl$_3$ NMR.[8,9] The exo hydrogens at δ 4.28 were shifted upfield as complexation with Eu(fod)$_3$-d_{27} took place. The aromatic hydrogens underwent no apparent shift. In order to determine complexation to be with the bridged carbonyl and not the imide carbonyls, the NMR of I with Eu(fod)$_3$-d_{27}–CDCl$_3$ was studied. The exo hydrogens at δ 4.26 underwent no apparent shift with Eu(fod)$_3$-d_{27}.[10]

The inclination for endo addition was ascribed by Alder and Stein[11] to the "maximum accumulation of double bonds". A quantum chemical restatement in terms of "secondary orbital interactions"[12] has emphasized the opinion[13–17] that secondary attractive forces in operation between centers not involved in eventual bond formation in the adduct account for the rule of endo addition.

There have been suggestions for the relative unimportance of secondary orbital relationships in favor of a steric repulsion hypothesis.[18–22] In the past decade, there have been several reports of exo adducts formed from the addition of *N*-phenylmaleimide to heterocyclic dienes.[1–4] The heteroatoms, each having at least one pair of nonbonded electrons, can participate in a secondary orbital effect leading to transition states which give rise to exo adducts. The carbonyl of 2,3,4,5-tetraphenylcyclopentadienone apparently does not sufficiently participate in secondary overlap in the transition state to form an exo adduct (instead, II is formed).

Experimental Section

***endo*-1,2,3,4-Tetraphenylbicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic Acid *N*-Phenylimide (I).** A solution of 5.000 g (0.0135 mol) of 1,2,3,4-tetraphenylcyclopentadiene and 2.48 g (0.014 mol) of *N*-phenylmaleimide in 100 ml of dry xylene was refluxed for 3–48[23] hr and cooled, and solid was recrystallized twice (first from *p*-xylene, second from anhydrous ethanol) to give 5.36 g (73%) of colorless crystals (the endo isomer): mp 241°; NMR, vide supra.

Anal. Calcd for $C_{39}H_{29}NO_2$: C, 86.16; H, 5.38; N, 2.58. Found: C, 86.42; H, 5.36; N, 2.61.

***endo*-1,2,3,4-Tetraphenylbicyclo[2.2.1]hept-2-en-7-one-5,6-dicarboxylic Acid *N*-Phenylimide (II).** A solution of 5.000 g (0.0130 mol) of 2,3,4,5-tetraphenylcyclopentadienone and 2.57 g (0.015 mol) of *N*-phenylmaleimide in 100 ml of dry xylene was refluxed for 3–48[23] hr and cooled, and the colorless crystals which separated were collected by filtration and recrystallized once from *p*-xylene to give 4.21 g (58%) of the endo isomer: mp 226°; NMR, vide supra.

Anal. Calcd for $C_{39}H_{27}NO_3$: C, 84.00; H, 4.88; N, 8.61. Found: C, 83.83; H, 5.17; N, 2.61.

Acknowledgment. The author wishes to thank the American Philosophical Society for its generous support.

Registry No.—I, 57066-03-2; II, 57128-65-1; *N*-phenylmaleimide, 941-69-5; 1,2,3,4-tetraphenylcyclopentadiene, 15570-45-3; 2,3,4,5-tetraphenylcyclopentadienone, 479-33-4.

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