$C\pi \rightarrow \pi^*$ Transition. II.[1a] Intramolecular Charge-Transfer Interactions across Space[1b]

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Abstract: In aqueous solutions, the uv spectra of diethyl esters of phenylmalonate, benzylmalonate, 2-phenethylmalonate, phenoxymalonate, *N*-methylanilinomalonate, benzamidomalonate, *p*-nitrophenoxymalonate, and 2,4-dinitrophenoxymalonate together with *N,N*-dimethylaniline, *p*-nitroaniline, and 2,4-dinitroaniline have been determined under neutral and alkaline conditions at ambient temperature. In these compounds, the phenyl or nitrophenyl moieties are separated from the malonate moiety by $-(CH_2)_n-$, –O–, or –N–, and –CONH– bridges in order to study the effects of distance, heteroatom, and functional group, respectively, on intramolecular charge-transfer interactions across space. The occurrence of these transitions is manifested as spectral changes in two wavelength regions. In the 240–260-nm region, new, intense peaks or general hyperchromism are evident in intramolecular charge-transfer or $C\pi \rightarrow \pi^*$ transitions, while in the long wavelength end (above 270 nm) of the spectra, absorption shoulders with $\epsilon < 700$ or general broadening are often observed. Compounds with the malonate moiety directly attached to the aromatic ring display only the new, intense absorption bands. Compounds with bridges show some degree of hyperchromism in the 240–260-nm region and absorption shoulders above 270 nm. These effects decrease with increasing separation. Bridges of heteroatoms exert subtle influences, the effects of which become quite pronounced in compounds with nitrogen bridges. Also, the ability of the NO_2 group to enhance the electron-accepting properties of the phenyl ring results in stronger interaction and, hence, increased intensities of charge-transfer bands.

An intramolecular $C\pi \rightarrow \pi^*$ transition has recently been identified in the uv spectra of the anionic forms of *N*-malonic esters of heteroaromatic compounds.[1a] It is characterized by the appearance of new, intense absorption bands ($\epsilon > 15{,}000$) or strong hyperchromism in the 240–260-nm region as compared with those of the undissociated molecules (Figure 1). These spectral changes were tentatively attributed to charge-transfer transitions involving excitation of a carbanion lone-pair electron to the π^* orbital of the heteroaromatic ring. Physical and chemical means of identifying $n \rightarrow \pi^*$ transitions are not readily applicable to these compounds since they are sparingly soluble in organic solvents and their anions can be generated only at extreme pH's. Although it is difficult to discriminate between this new transition and $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$, the data infer that the new transition differs from both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$.[1a] In order to elucidate this transition, studies are being extended to include carbocyclic derivatives. Compounds were selected in which phenyl or nitrophenyl moieties are linked to the malonate with $-(CH_2)_n-$, –O– or –N–, and –CONH– bridges in order to determine the effects of distance, heteroatom, and functional group, respectively, on intramolecular charge-transfer interactions across space.

Results and Discussion

Ordinarily, intramolecular charge transfer occurs with most benzene derivatives. In these compounds, the electron migration from the highest occupied level of the electron-donating aromatic moiety to the lowest vacant orbital of the acceptor, *i.e.*, the substituent groups, results in transition bands in the 190–260-nm region ($\epsilon \geq 4000$).[3,4] In the present study, charge-transfer transition also occurs; however, the electron migration is reversed, *i.e.*, from the malonate anion to the phenyl ring. A similar transition occurs with the malonate group substituted directly on the N atom of the heteroaromatic rings where the two moieties are in proximity for interaction and yet are not conjugated, an ideal situation for intramolecular charge-transfer interactions.[5] The latter two transitions are novel in that we know of no previous cases involving such a carbanion. Although a similar transition occurs in carboxylic acids and their esters, it involves the transfer of an electron from the oxygen atom of a hydroxy or an alkoxy group to the π^* orbital of the carboxyl moiety and results in the appearance of intense bands in the vacuum uv region.[6]

Effect of Distance. If the malonate group is directly attached to the aromatic phenyl ring, *i.e.*, diethyl phenylmalonate in its anionic form, the two moieties will be conjugated by charge-resonance mechanism.[7] One would observe bathochromic shifts accompanied by hyperchromism[8] in the electronic spectra of this type of

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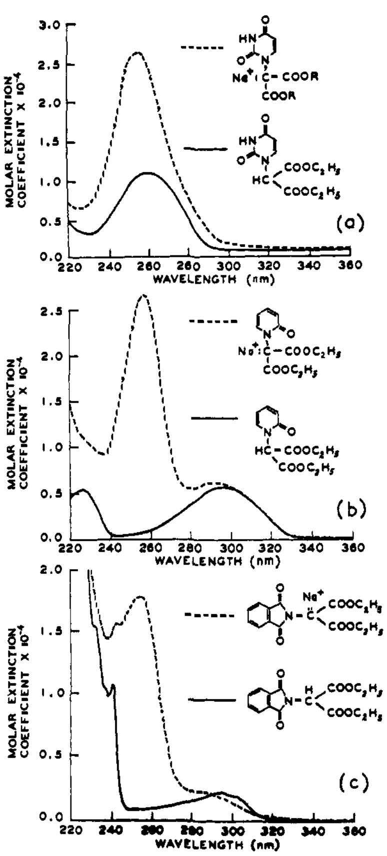

Figure 1. Uv spectra of (a) diethyl uracil-1-malonate, (b) N^1-(diethyl malonate)-2-pyridone, and (c) diethyl phthalimidomalonate.

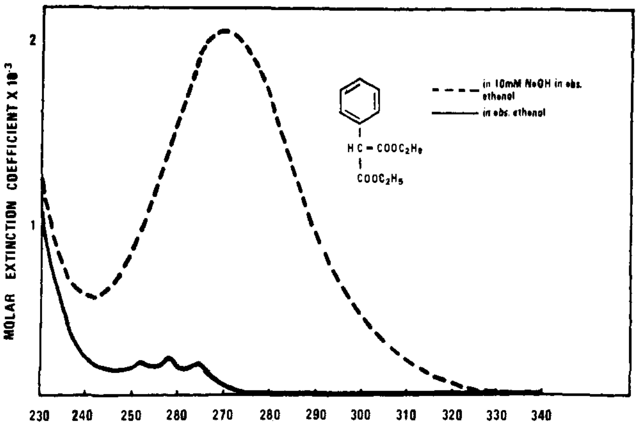

Figure 2. Uv spectra of diethyl phenylmalonate.

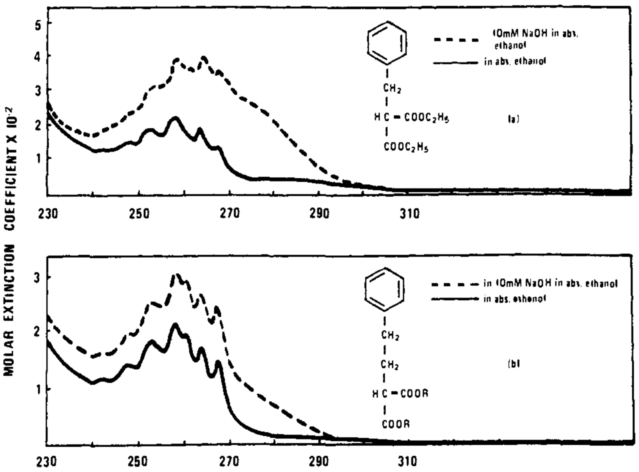

Figure 3. Uv spectra of (a) diethyl benzylmalonate and (b) diethyl 2-phenethylmalonate.

compound. Indeed, the anionic form of diethyl phenylmalonate shows a 10-nm red shift, with a tenfold increase in molecular absorbancy as compared with that of the neutral form (Figure 2). This hyperchromism may obscure the fact that the $C\pi \rightarrow \pi^*$ and the $\pi \rightarrow \pi^*$ bands may be present. [As discussed above, this charge resonance mechanism is probably unimportant in cases where the anionic forms of malonic esters are directly attached to the N atoms of the heteroaromatic nuclei[1a] as seen in their uv spectra (Figure 1).]

However, if the phenyl ring and the malonate group are separated by one or more methylene groups, the carbanion charge will probably be localized in the malonate moiety. Thus, the resonance mechanism is unlikely. It may then be possible to observe bands caused solely by charge transfer and by $\pi \rightarrow \pi^*$ transitions. As seen in Figure 3a, the uv spectrum of the anionic form of diethyl benzylmalonate differs from that of its neutral form in its twofold hyperchromism and its new shoulder at 270–290 nm ($\epsilon \sim 280$). Also evident is the structured spectrum which closely resembles the $\pi \rightarrow \pi^*$ transition of the neutral species. In Figure 3b, the uv spectra of diethyl 2-phenethylmalonate, $-(CH_2)_2-$, show characteristic changes similar to those observed in the benzyl, $-(CH_2)_1-$, derivative. However, there is a 50% reduction in the hyperchromism for the $C\pi \rightarrow \pi^*$ transition. Thus, as the distance between the donor and the acceptor increases, the effect is greatly diminished. On the other hand, one cannot eliminate the possibility that a maximal interaction may exist with an optimal separation, which is longer than $-(CH_2)_2-$ as in other systems.[9-11] This idea is currently being studied.

Notably, the positions and the intensities of these intramolecular $C\pi \rightarrow \pi^*$ transitions of phenyl alkyl derivatives of malonate [Figure 3, λ_{max} 270–300 nm (ϵ 100–280)] differ considerably from those of N-malonic esters of heteroaromatic compounds [Figure 1, λ_{max} 240-260 nm ($\epsilon > 15{,}000$)]. Further study in progress is aimed at understanding this difference between heteroaromatic and aromatic compounds. Indeed, spectral changes observed for the latter are similar to those observed for intramolecular charge-transfer transitions in several systems including chemically modified chymotrypsin,[12] N-[ω-(p-nitrophenyl)alkyl]aniline,[9] and diphenylmethane derivatives.[10] It is likely that their mechanisms are also similar.

Effect of Heteroatoms. When the donor and the acceptor moieties were separated by a heteroatom, effects similar to those of the methylene groups were observed. As compared with the neutral form, the anionic form of diethyl phenoxymalonate (Figure 4) shows the same structured spectrum for $\pi \rightarrow \pi^*$ transition and the enhancement of the absorption bands with the appearance of a shoulder at 280–300 nm ($\epsilon \sim 700$). This enhancement is about three to five times as intense

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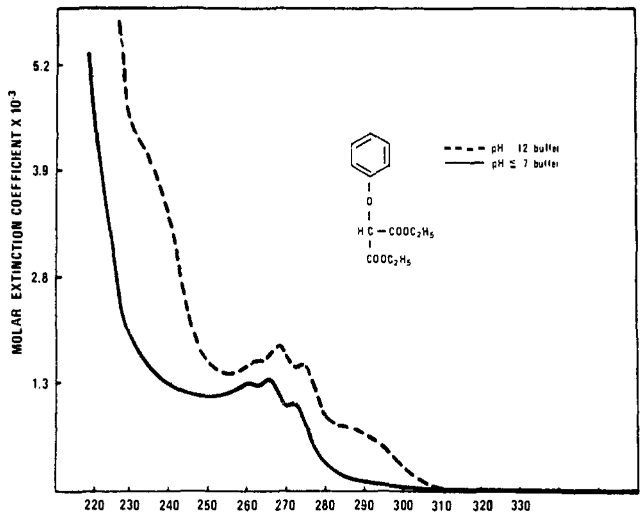


Figure 4. Uv spectra of diethyl phenoxymalonate.

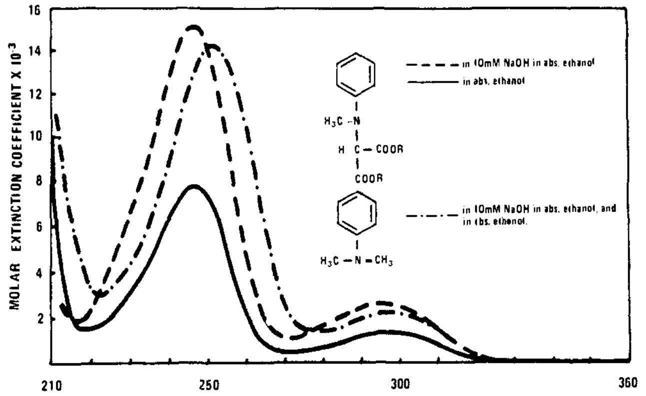


Figure 5. Uv spectra of N,N-dimethylaniline and diethyl N-methylanilinomalonate.

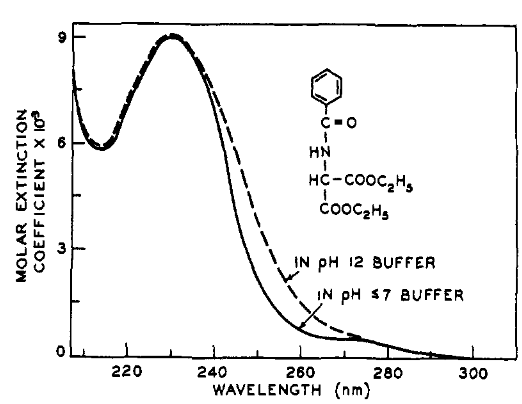


Figure 6. Uv spectra of diethyl benzamidomalonate.

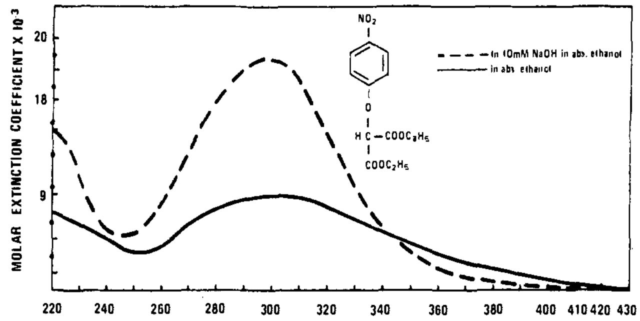
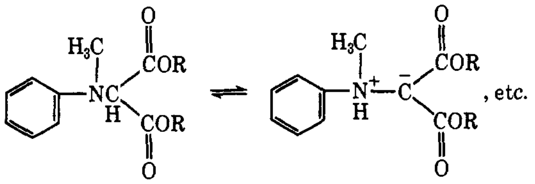


Figure 7. Uv spectra of diethyl p-nitrophenoxymalonate.

as that of the methylene bridge, suggesting that an oxygen bridge is more effective in this type of charge-transfer transition. To our knowledge, this represents the *first* documentation of such interactions operating through an oxygen bridge. It is probable that similar results would be obtained for compounds with a sulfur bridge. Significantly, these effects are not caused by the interaction of the lone-pair electrons (l) of the oxygen atom with the aromatic ring, as shown by their absence in anisole[13] either in absolute ethanol or in the basic solvent. However, the intense shoulder at 240 nm in the spectrum at pH 12 appears to be an l → π* transition band.

The effects of a nitrogen bridge were also studied. The uv spectra of N,N-dimethylaniline and diethyl N-methylanilinomalonate were compared (Figure 5). The former showed no spectral change in base or absolute ethanol and had two maxima at 296 nm (ϵ 2.08 × 10^3) and 251 (14.3 × 10^3).[14] For the latter, two absorption maxima were observed at 296 nm (ϵ 1.80 × 10^3) and 248 (7.80 × 10^3) in absolute ethanol and at 294 nm (ϵ 2.40 × 10^3) and 246 (15.2 × 10^3) in the basic solvent. Thus, the hypsochromic shifts and hyperchromism noted of the latter in the basic solvent are analogous to those observed with diethyl uracil-1-malonate and again suggest some charge-transfer interaction. Interestingly, the spectral differences observed in the two compounds in absolute ethanol may be attributed to the possible existence of the zwitterionic species as shown below.



This ionic species should be predominant in ethanolic solution since the pK_a of this malonate derivative is 4.85. This would account for reduced absorption of the malonate compound as compared with $-N(CH_3)_2$ which is a strong electron donor and the charge transfer which could occur from the nitrogen lone pair.

Effect of a Functional Group. In diethyl benzamidomalonate, where an amide bridge separates the malonate from the aromatic moiety, the uv spectrum of the anionic form differs from that of the neutral form. There is a slight broadening in the long wavelength portion of the absorption spectrum, Figure 6. This may again be attributed to charge-transfer effects. The weak interaction is probably due to the greater distance (see Table I) between the donor and the acceptor and is similar to that observed in Figure 3b. However, some subtle influence on this transition by the presence of the carbonyl group cannot be ruled out.

Effects of Substituents on the Acceptor. To further demonstrate that the phenyl ring is the acceptor, diethyl p-nitrophenoxymalonate and diethyl 2,4-dinitrophenoxymalonate were synthesized and studied. For com-

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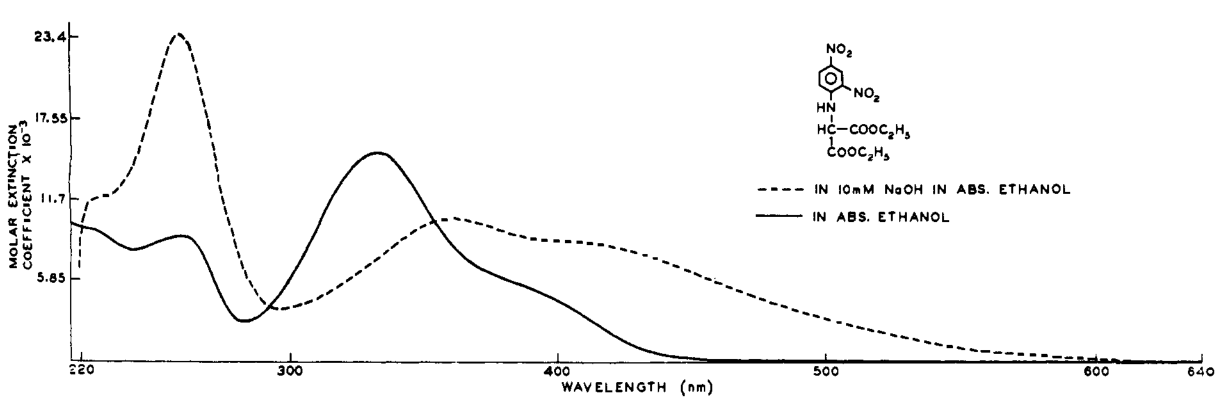

Figure 8. Uv spectra of diethyl 2,4-dinitroanilinomalonate.

parison purposes, *p*-nitroanisole and 2,4-dinitroaniline were also examined.

For *p*-nitroanisole, uv spectra in absolute ethanol and in the basic solvent are the same.[15] For *p*-nitrophenoxymalonate, the formation of carbanion in the basic solvent is accompanied by 2.2-fold hyperchromism, Figure 7. Here, the charge-transfer bands from $C\pi \rightarrow \pi^*$ and from phenyl to $-NO_2$ moieties overlap the $\pi \rightarrow \pi^*$ band of the neutral form and compare to those observed in uracil-1-malonate (Figure 1a). Comparison of the hyperchromism increases with those observed for phenoxymalonate (Figure 4) indicates that a nitro group would enhance the electron-accepting properties of the phenyl moiety and result in more intense charge-transfer interactions.[16]

Table I. Effect of Various Groupings between the Aromatic and Malonate Moieties of Intramolecular Charge-Transfer Bands

Diethyl malonate derivatives	Type of bridge	Separation, Å[a]	Charge-transfer bands: Intense, sharp (245–260 nm)	Charge-transfer bands: Shoulder, ϵ (above 270 nm)
Uracil-1	None	1.48	Max 254	
2-Pyridone N^1-	None	1.48	Max 257	
Phthalimido	None	1.48	Max 254	
Phenoxy	-O-	2.86	Hyperchrom	700 (280–300)
[*p*-Nitrophenoxy]	-O-	2.86	[Hyperchrom]	[298 sharp]
N-Methylanilino	-N-	2.91	Max 246	294
[2,4-Dinitroanilino]	-N-	2.91	[Max 261]	[420–600]
Benzyl	$-CH_2-$	3.03	Slight hyperchrom	280 (270–300)
2-Phenethyl	$-CH_2CH_2-$	4.57	Slight hyperchrom	100 (270–290)
Benzamido	-CONH-	4.31		Slight broadening

[a] "Handbook of Chemistry and Physics," 48th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1968, p 148.

More dramatic changes were observed in the uv spectrum of the anionic form of 2,4-dinitroanilinomalonate, Figure 8. For the neutral form, there are absorption maxima at 261 nm (9.2 × 10^3) and at 333 (15.3 × 10^3) and a shoulder at around 400 nm. However, the carbanion form shows a 2.5-fold hyperchromicity at 261-nm peak (ϵ 23.5 × 10^3), a shift of the 333 peak to 362 nm with reduced intensity (ϵ 10.5 × 10^3), and a fairly intense, broad absorption appearing at 420–600 nm. [The uv spectrum of 2,4-dinitroaniline [17] shows a new, broad absorption at 420–600 nm, a shoulder in the 400-nm region, and a slight enhancement of the band at 330 nm, but *no* change in the 260-nm region when determined in basic solvent as compared with that in absolute ethanol.] Thus, it is reasonable to suggest that $C\pi \rightarrow \pi^*$ transition between the malonate anion and the 2,4-dinitrophenyl ring are responsible for the 2.5-fold hyperchromicity and 30-nm bathochromic shift discussed above. However, the spectral changes observed at wavelengths >400 nm may suggest intermolecular charge-transfer interactions between nitro groups and aromatic rings[16] or between the nitro group and the base or the solvent.[17] In Figure 5, similar interactions leading to hyperchromism at 246 nm were observed in *N*-methylanilinomalonate. The more dramatic changes observed in Figure 8 indicate that the electron-withdrawing property of the nitro group again enhances the electron-accepting properties of the phenyl ring.

Since charge-transfer transition absorption bands appeared in about the same wavelength region (240–260 nm) for both phenoxymalonate and its *p*-nitro derivative and for both anilinomalonate and its 2,4-dinitro derivative, it is unlikely that the acceptors for the two sets are the phenyl ring and the nitro group, respectively. Rather, the aromatic ring is the acceptor in both cases. Again, for this band, charge-transfer interactions involving lone-pair electrons of oxygen and nitrogen may be ruled out since anisole, *p*-nitroanisole, *N*,*N*-dimethylaniline, and 2,4-dinitroaniline do not show charge-transfer effects in this region. Also, intermolecular charge-transfer effects may be unimportant in these dilute solutions since their absorption follows Beer's law.

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Conclusion

In short, charge-transfer transitions occurring in the anionic forms of malonic esters of heteroaromatic and aromatic compounds are manifested as spectral changes in two wavelength regions (Table I). In the 240–260-nm region, new, intense peaks or general hyperchromism are evident in intramolecular charge transfer or $C\pi \rightarrow \pi^*$ transitions, while in the long wavelength end (above 270 nm) of the spectra, absorption shoulders with $\epsilon < 700$ or general broadening are often observed. In general, compounds with the donor and the acceptor moieties directly attached to one another show little effect in the long wavelength region. However, new, intense absorption bands are conspicuous. Compounds with various bridges show some degree of hyperchromism in the shorter wavelength region and absorption shoulders in the long wavelength region. These effects decrease with increasing separation between the two moieties. Very little effect can be observed with benzamido derivatives, where the separation by –CONH– is somewhat less than that by the $-CH_2CH_2-$ bridge. This evidence suggests that heteroatoms exert certain subtle influences, the effects of which become quite pronounced as in the cases of compounds with a nitrogen bridge. Also, the electron-withdrawing NO_2 groups on phenyl rings increase the capability of the acceptor to accept the electron; the result is stronger interaction with the donor moiety. Thus, the intensities of the charge-transfer bands increase accordingly.

Experimental Section

Ultraviolet Spectra. Ultraviolet absorption spectra were recorded on a Cary recording spectrophotometer, Model 14, at ambient temperature. Malonic ester derivatives of heterocyclic and carbocyclic compounds were measured in pH ≤ 4 buffered aqueous solutions and the spectra of their anionic forms were determined in pH 12 buffered aqueous solutions. Those of the water-insoluble compounds were obtained in absolute ethanol and 0.01 *M* NaOH in absolute ethanol, respectively.

Syntheses. Diethyl uracil-1-malonate and diethyl *N*-methylanilinomalonate were prepared using the methods reported earlier.[1a]

Diethyl 2,4-dinitroanilinomalonate was synthesized according to the method of Harnik and Margoliash,[18] mp 103° (lit. 102.5–103.5°).

Diethyl phenoxymalonate was prepared by mixing sodium phenoxide (0.1 *M*, 11.6 g) and diethyl bromomalonate (0.1 *M*, 26.3 g) in a flask equipped with a thermometer and a reflux condenser bearing a $CaCl_2$ tube. Vigorous reaction occurred and the temperature rose to 120°. Upon completion of the reaction the temperature dropped to 60°. The reaction mixture was kept at 80° for 1 hr. After the mixture was cooled, the product was extracted several times with anhydrous ether. The ether was removed from the combined extracts and the residue was then subjected to fractional distillation. The fraction distilled at 130–170° (5 mm) was collected. Redistillation of this fraction gave 11 g of material with bp 147–150° (5 mm). *Anal.* Calcd for $C_{13}H_{16}O_5$: C, 61.90; H, 6.31. Found: C, 62.03; H, 6.25; mol wt, *m/e* 252 (mass spectrum).

Diethyl *p*-nitrophenoxymalonate was synthesized by the reaction of equimolar amounts of sodium *p*-nitrophenoxide and diethyl bromomalonate in dimethylformamide using a procedure described for diethyl uracil-1-malonate. The crude product (~80%) was purified by crystallization in absolute ethanol to constant mp 63–64°. *Anal.* Calcd for $C_{13}H_{15}O_7N$: C, 52.52; H, 5.05; N, 4.71. Found: C, 52.48; H, 5.00; N, 4.67; mol wt, *m/e* 297 (mass spectrum).

Diethyl phenylmalonate, diethyl benzylmalonate, and diethyl 2-phenethylmalonate, obtained from Aldrich Chemical Co., were redistilled and only the middle fractions boiling at 170–171° (14 mm),[19] 162–163° (10 mm),[19] and 180–181° (16 mm),[20] respectively, were used for the spectral determinations.

Diethyl benzamidomalonate, obtained from Chemical Procurement Lab. Inc., was recrystallized to constant mp 61–62° (lit.[19] 61°).

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Halogen Atom Charge-Transfer Complexes in the Vapor Phase

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Abstract: Transient absorption has been detected following the flash photodissociation of iodine in benzene, cyclohexane, methyl iodide, ethyl iodide, methyl bromide, ethyl bromide, methyl chloride, and ethyl chloride and similarly with bromine in the same alkyl bromides and chlorides and in xenon. The correlation between the spectral band maxima and the ionization potentials of the donor species clearly indicate the charge-transfer character of these spectra. The bands are blue shifted from those of the comparable liquid-phase species, although the interaction energies appear to be about the same. The data do not distinguish between complex and collisional or contact charge transfer between the iodine or bromine atoms and the various donor species, but in combination with vapor-phase third-order atom recombination rates the results are consistent with predominantly complex interactions.

Many studies have recently been reported on vapor-phase molecular iodine charge-transfer (CT) complexes.[1–10] In general, the absorption maximum of the CT band shifts to the blue, the formation constant (*K*) increases, and the extinction coefficient (ε) de-

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