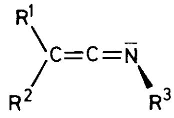
Electronic Spectra and Electronic Structures of Ketenimines and Carbodi-imides

By **Wolfgang Kosbahn,** Institut für Physikalische und Theoretische Chemie der Technischen Universität München, Germany
Wolfgang Runge,*,† Organisch-Chemisches Institut der Technischen Universität München, Germany

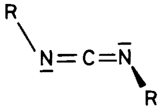
U.v. absorption spectra of ketenimines (>C=N=N–) and carbodi-imides (–N=C=N–) with phenyl and alkyl groups as substituents are reported. Band assignments are achieved by relying primarily on comparisons with structurally related molecules, in particular allenes (>C=C=C<), isocyanates (–N=C=O), and imines (>C=N–). More detailed information about the excited singlet states of the molecules is deduced from semiempirical CNDO/S–CI calculations. These calculations are also used for a description of the electronic structures of ketenimines and carbodi-imides in terms of molecular orbitals and electron density distributions.

DURING the last two decades the properties of ketenimines and carbodi-imides have become topics of major chemical interest.[1-3] Their ^{1}H,[4,5] ^{13}C,[6-8] and ^{15}N [8] n.m.r. spectra have been intensively investigated.[3] The electronic spectra (and, more generally, electronic structures in terms of molecular orbitals and electron density distributions) have, however, received little attention.[3] The present work has been undertaken to remedy, at least partly, this situation. In particular, more detailed knowledge of the electronic structures and electronic excited states of ketenimines and carbodi-imides may help in rationalizing the observed unusual upfield ^{15}N chemical shifts of such compounds [8] when compared with those of imines.

In the present contribution the electronic ground state and low energy excited (singlet) states of ketenimines and carbodi-imides (1)—(14) with alkyl and phenyl substituents are investigated by means of u.v. absorption spectroscopy [(5)—(8), (10), (12)] and semiempirical CNDO/S calculations [(1)—(4), (8), (9), (11), (13), (14)]. Furthermore, our results are related to several current literature debates concerning the triatomic cumulenes, an isoelectronic series of molecules,[3, 9-12] referring in particular to allenes and isocyanates.



	R¹	R²	R³
(1)	H	H	H
(3)	CH_3	CH_3	CH_3
(5)	C_2H_5	CH_3	$CH(CH_3)C_2H_5$
(7)	C_2H_5	H	C_6H_5
(9)	CH_3	CH_3	C_6H_5
(10)	C_2H_5	CH_3	C_6H_5
(11)	C_6H_5	CH_3	CH_3
(12)	C_6H_5	CH_3	$CH(CH_3)C_2H_5$
(13)	C_6H_5	H	CH_3
(14)	H	H	C_6H_5



	R
(2)	H
(4)	CH_3
(6)	$(CH_3)_3C$
(8)	C_6H_5

Close relationships among the molecules under consideration are also guaranteed on the structural level, as ketenimines and carbodi-imides, at least those with substituents bonded *via* carbon to the cumulene skeletons, have allene-like geometries with the substituents in perpendicular planes.[13]

In theoretical studies of the electronic structures of azacumulenes the emphasis has been mostly on the geometries and barriers to stereoisomerization of ketenimine (1) and carbodi-imide (2).[9,14] However, owing to tautomerism with acetonitrile ($CH_3C{\equiv}N$) and cyanamide ($H_2NC{\equiv}N$), respectively, (1) and (2) cannot be isolated and are of minor chemical interest.

U.v. spectra of some azacumulenes have been published.[15,16] However, for dimethylcarbodi-imide (4) a band assignment has been suggested [16a] which we feel necessary needs to be partly revised. Additionally, some photoelectron (p.e.) spectroscopic data for ketenimines [17] and carbodi-imides [18] are available. These p.e. data will be used in conjunction with our theoretical CNDO/S investigation to describe the electronic structures of the azacumulenes in terms of molecular orbitals.

EXPERIMENTAL AND COMPUTATIONAL

Syntheses of compounds (5)—(7), (10), and (12) are described in refs. 6*b* and 18*a*. They were purified by vacuum distillation just prior to measurement. Compound (8) (and its u.v. spectrum) was kindly provided by Prof. J. C. Jochims (Konstanz, Germany).

Solution spectra [in n-hexane (Uvasol; Merck)] were measured at 300 K either with a PMQ II Zeiss spectrophotometer [(5), (7), (10), (12)] or a Cary 14 spectrometer [(8)]. Spectral resolution was *ca.* 50 cm^{-1} at 40 000 cm^{-1} and *ca.* 120 cm^{-1} at 50 000 cm^{-1}.

The vacuum u.v. spectrum of (6) was run with a double beam 1 m model 225 McPherson vacuum u.v. spectrometer using a hydrogen discharge source. Th ε values of (6) are considered as good approximate values, but are not useful for quantitative purposes.

Semiempirical all-valence electron CNDO/S-CI calculations were done as described in refs. 10*a* and *c* assuming 'standard' bond lengths r and bond angles α for the substituents and the ketenimine and carbodi-imide skeletons

---

† *Present address:* SfS, Werderstrasse 35, D-6900 Heidelberg, Germany.

($r_{C=C}$ 1.33, r_{N-H} 1.00, $r_{C=N}$ 1.23 Å, $\alpha_{C=N-C}$ 125°, $\alpha_{H-C-H} = \alpha_{H-C-C} = \alpha_{C-C-C} = 118°$).[12] Methyl group conformations were selected in accord with those observed for allenes and ketens,[12] *i.e.* the methyl groups have C_s site symmetries with one hydrogen eclipsing the double bond. The definition of molecule-fixed Cartesian axes is: x-axis coinciding with the N=C=X (X = C, N) axis; for ketenimines the substituents at the terminal carbon atom are situated in the xy plane. In (11) the phenyl group is twisted by 20° relative to the xy plane, by analogy with the situation in α-methyl-(phenyl)allenes.[12]

In most cases, configuration interaction (CI) was limited to the first 30 monoexcited configurations.

RESULTS AND DISCUSSION

(1) *U.v. Absorption Spectra.*—In Figures 1 and 2 the solution u.v. spectra of the ketenimines (5), (7), (10), and (12) and diphenylcarbodi-imide (8) are displayed. The u.v. absorption characteristics (and band assignments) are summarized in Table 1. The spectra are characterized by low to medium intensity bands at lowest energies followed by rather intense bands. Sometimes the lowest energy bands appear only as shoulders.

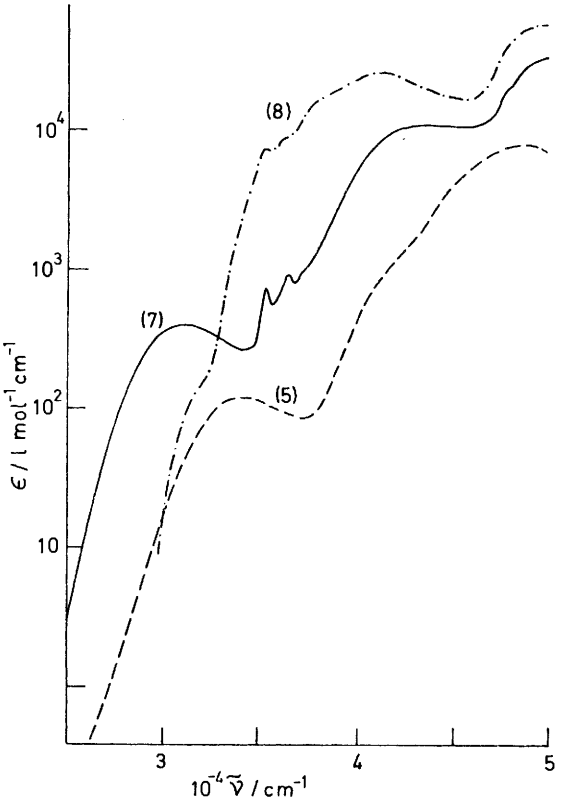


FIGURE 1 U.v. absorption spectra of ketenimines (5) and (7) and carbodi-imide (8) (in n-hexane)

The band assignments for the trialkylketenimine (5) and the N-phenylketenimines (7) and (10) rely on correlations with corresponding bands or excited states, respectively, in trimethylketenimine (3) and N-phenyl-(dimethyl)ketenimine (9), as it may be assumed generally that different alkyl groups exhibit very similar substituent effects on orbital energies or excited states energies, respectively. Compounds (3) and (9) have C_s symmetries which hence allow a strict $\pi(a'')$ — $\sigma(a')$ separation of the MOs. Correspondingly, all excited singlet states transform according to the irreproducible representations A' and A''. $^1A'$ Excited states result from electric dipole-allowed transitions and therefore should be associated with strong u.v. bands. $^1A''$ Excited states result from electric dipole-forbidden, magnetic dipole-allowed transitions and hence should be associated with weak u.v. bands.

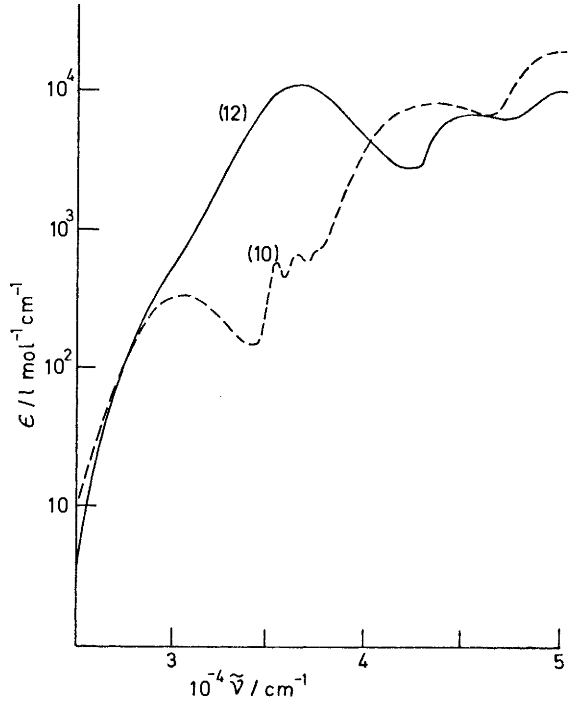


FIGURE 2 U.v. absorption spectra of ketenimines (10) and (12) (in n-hexane)

For the interpretations of the u.v. bands a crude description of the electronic structures of the molecules (which will be refined in subsequent sections) in terms of simple valence-bond functions suffices. The highest occupied molecular orbital (HOMO) of ketenimine (1) is expected to be composed of the lone-pair n_N at the nitrogen atom (as in imines)[19] and the C=C π_z-type orbital, *i.e.* according to symmetry the HOMO in (1) [and also in (3)] is a $\sigma(a')$ orbital. By analogy with the situation in allenes,[3,9,10] the outermost (occupied) σ orbitals of ketenimines are termed $\bar{\pi}_{(1)}(a')$ [$\bar{\pi}_{(-1)}(a')$ being the lowest unoccupied σ orbitals (σ LUMOs)].

The second occupied orbital in ketenimine (1) (or alkylated derivatives) should be the $\pi_{(1)}(a'')$ orbital which is expected to consist essentially of the C=N (p_y) double bond. The $\bar{\pi}_{(2)}(a')$ orbital should be more stable than the π HOMO. Therefore, the lowest energy excited states of alkylated ketenimines are expected to originate with the σ and π HOMOs ($\bar{\pi}_{(1)}$, $\pi_{(1)}$).

From the relatively low intensities of the longest wavelength u.v. bands of (5), (7), and (10) in the range 30 000—35 000 cm^{-1} one may conclude that these bands correlate with $^1A''$ excited states in the dimethylketenimines (3) and (9). The substituent effects of the alkyl groups in the *N*-phenylketenimines (7) and (10) may be used to assign the particular electronic transition from which the corresponding $^1A''$ excited states result. As alkyl groups do not affect significantly energies of unoccupied orbitals, but destabilize occupied orbitals by 0.5—0.7 eV,[3,10] the bathochromic shift of the longest wavelength u.v. bands comparing the monoalkyl (7) and dialkyl compounds (10) indicates that the lowest energy electronic transitions originate with the σ HOMOs, *i.e.* the longest wavelength u.v. bands in (5), (7), and (10) should result from σ,π* excitations and should be associated with $^1A''(\bar{\pi}_{(1)}, \pi_{(-1)})$ excited states in (3) and (9), respectively.

TABLE 1

U.v. absorption characteristics and band assignments of ketenimines and carbodi-imides

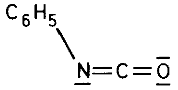
Excited state	$\tilde{\nu}$/cm^{-1}	ε/l mol^{-1} m^{-1}
N-s-Butyl(ethyl)(methyl)ketenimine (5)		
$^1A''(\bar{\pi},\pi^*)$	34 300	112
$^1A''(\pi,\bar{\pi}^*)$	41 600	1 000
$^1A'(\bar{\pi},\bar{\pi}^*)$	48 700	6 460
N-Phenyl(ethyl)ketenimine (7)		
$^1A''(\bar{\pi},\pi^*)$	31 000	257
$^1A'(B_{2u})$	35 400	562
	36 300	912
	37 000	1 047
$^1A'(B_{1u})$	43 000	10 590
$^1A'(E_{1u(a)})$	48 000	15 850 [a]
$^1A'(E_{1u(b)})$	50 000	21 900
N-Phenyl(ethyl)(methyl)ketenimine (10)		
$^1A''(\bar{\pi},\pi^*)$	30 000	230
$^1A'(B_{2u})$	35 300	560
	36 300	1 000
	37 500	1 072
$^1A'(B_{1u})$	43 000	11 750
$^1A'(E_{1u(b)})$	50 000	23 200
N-s-Butyl(methyl)(phenyl)ketenimine (12)		
$^1A''(\pi,\bar{\pi}^*)$	29 000	400 [a]
$^1A'(B_{1u})$	36 250	25 700
$^1A'(E_{1u(a)})$	43 000	9 440
$^1A'(E_{1u(b)})$	50 000	13 200
Dimethylcarbodi-imide (4) [b,c]		
$^1A(A_2)$	38 450	138
	39 400	229
	40 450	348
$^1B(B_1)$	44 000	1 000 [a]
$^1A(A_1)$ $(b(a),3s)$	48 400	
$^1B(B_2)$ $(b(a),3p)$	54 300	26 000
	58 000	10 000 [d]
$(b(a),3d)$	62 500	30 000
Diphenylcarbodi-imide (8)		
^1B ^1A	31 500	100
$^1B(B_{2u})$ $^1A(B_{2u})$	35 350	7 080
	36 350	8 990
	38 000	14 000
$^1B(B_{1u})$ $^1A(B_{1u})$	41 320	25 230
$^1A(E_{1u(a)})$ $^1B(E_{1u(a)})$ $^1B(E_{1u(b)})$ $^1A(E_{1u(b)})$	50 000	57 000

[a] Shoulder. [b] From ref. 16*a*. [c] Bands with $\tilde{\nu} \geqslant 50\,000$ cm^{-1} are from the gas-phase spectrum of (6). [d] See text.

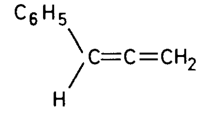
The bathochromic shift of the $^1A''$ $(\bar{\pi}, \pi^*)$ band in (10) relative to that in (5) is due to the stabilization of the π* orbital through the π conjugative effect of the phenyl group. Then, the weak shoulder observed near 41 600 cm^{-1} in the u.v. spectrum of (5) should result from the π, σ* transition, *i.e.* should correspond to the $^1A''$ $(\pi, \bar{\pi}^*)$ excited state in (3). Owing to its intensity the relatively strong u.v. band of (5) at 48 700 cm^{-1} must be associated with a $^1A'$ excited state. For energetic reasons the corresponding electronic excitation should involve essentially the HOMO and the LUMO, *i.e.* the 48 700 cm^{-1} band in (5) should correspond to the $\bar{\pi}$, $\bar{\pi}^*$ transition in (3) [excited state $^1A'$ $(\bar{\pi}, \bar{\pi}^*)$].

These results show that as regards the excited states the structurally related ketenimines $R_2C{=}C{=}NR$ and imines $R_2C{=}NR$ are quite different. For instance, compared with the *n*,π* transition in imines such as $(CH_3)_2CHCH{=}NC_2H_5$ [with $\tilde{\nu}(n,\pi^*)$ 41 000 cm^{-1}],[19a] the longest wavelength transition in ketenimines [such as (5)] which also originates with an orbital containing the nitrogen lone-pair is bathochromically shifted by almost 1 eV (to *ca.* 34 000 cm^{-1}).

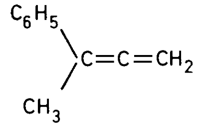
The interpretations of the u.v. spectra of the *N*-phenyl-substituted ketenimines are straightforward, relying on comparisons with phenyl isocyanate (15),[12b,c] phenylallenes (16) and (17),[11a,b,c,] and *N*-phenylaldimines.[19c,d]



(15)



(16)



(17)

In general, the symmetry lowering on attaching a substituent to benzene can be regarded as a perturbation to the local high symmetry of the aromatic ring, thus retaining the benzene parentage in the phenyl derivatives to a large extent.[10a,19d] Therefore, the excited states of the phenylketenimines may be advantageously correlated with the low energy excited states of benzene.[20]

The medium intensity u.v. bands in the *N*-phenylketenimines (7) and (10) at *ca.* 35 400 cm^{-1} with vibrational progressions of *ca.* 1 000 cm^{-1} are clearly associated with $^1A'$ excited states correlating with $^1B_{2u}$ in benzene. These excited states $^1A'(B_{2u})$ result from π, π* excitations which are largely localized on the phenyl ring. Therefore, their spectral positions are unaffected by perturbations of the different atoms X, Y, and Z in $C_6H_5X{=}Y{=}Z$ systems. Almost identical u.v. absorptions (including vibrational fine structures) as in (7) and (10) are observed for phenyl isocyanate (15) [12b,c] and phenylallene (16).[10a] Therefore, by analogy with the assignment given for (15) we associate the 35 400 cm^{-1} bands in the N-phenylketenimines with the 0,0 transitions.

On the other hand, the strong intensities of the u.v. bands near 43 000 cm^{-1} in (7) and (10) and their almost identical positions with the '$^1B_{1u}$ state' in phenyl isocyanate (15) ($\tilde{\nu}$ 44 000 cm^{-1})[12b] form a sound basis for the assignments of the 43 000 cm^{-1} bands in (7) and (10) to the $^1A'(B_{1u})$ excited states which are expected to result essentially from $\pi_{(1)}$, $\pi_{(-1)}$ transitions.

As usually observed when an α-carbon atom in a $C_6H_5CH{=}X$ system is replaced by nitrogen (*e.g.* styrenes *versus* N-phenylaldimines)[19c,20] the $^1A'(B_{1u})$ bands in N-phenylketenimines are hypsochromically shifted by *ca.* 4 000 cm^{-1} relative to the corresponding 'B_{1u} bands' in phenylallenes such as (16) or (17).[10a] By analogy with the phenylallenes the u.v. shoulder observed at *ca.* 48 000 cm^{-1} in (7) and the maxima at 50 000 cm^{-1} in (7) and (10) are associated with $^1A'(E_{1u(b)})$ and $^1A'(E_{1u(a)})$ excited states.

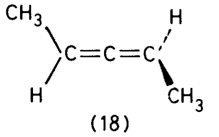
In N-phenyl(dimethyl)ketenimine (9) of C_s symmetry the phenyl $\pi(b_1)$ and $\pi(a_2)$ orbitals retain their $\pi(a'')$ character strictly on conjugation with the corresponding orbitals of the cumulene subunit. On the other hand, C-phenylketenimines, such as (11) or (12), have no (geometrical) mirror plane and, therefore, referring to the symmetry (C_1) of such molecules the $\pi - \sigma$ separabilities of their MOs are expected to break down. However, owing to the large energy gaps between the outermost (π and $\bar{\pi}$) orbitals of the constituent subunits (C_6H_5 and C=C=N) in terms of perturbation theory π–σ mixing (or π–$\bar{\pi}$ mixing, respectively) is expected to be small (see later). This means that the outermost orbitals of C-phenylketenimines may be classified according to their (approximate) nodal properties as π [comprising the phenyl group π system and the HOMO of the C=C=N fragment which is $\bar{\pi}_{(1)}(a')$ in (3)] and $\bar{\pi}$ [being essentially the C=N π bond, $\pi_{(1)}(a'')$ in (3)].

Taking this into account the band assignment for the u.v. spectrum of the C-phenylketenimine (12) given in Table 1 is obvious. Notably, the intense u.v. band at 36 250 cm^{-1} [$^1A'(B_{1u})$] is bathochromically shifted relative to the B_{1u} bands of the phenylallenes (16) and (17) by *ca.* 4 000 cm^{-1}. The $^1A'(B_{1u})$ band of (12) is expected to bury the medium $^1A'(B_{2u})$ band which should be located at the same spectral position as in (10) (see Figure 2).

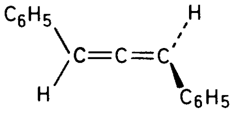
Another remarkable feature of the u.v. spectrum of (12) when compared with those of (10) or (16), respectively, is the relatively large energy gap (*ca.* 0.8 eV) between the u.v. bands associated with the excited states $^1A'(E_{1u(a)})$ and $^1A'(E_{1u(b)})$. In (10) and (16) these last bands or excited states, respectively, lie much closer to each other.

Turning to the interpretation of the u.v. spectra of the carbodi-imides an essential difference when compared with the situation in ketenimines is that, owing to the C_2 rotational symmetries, a $\pi - \sigma$ separation of the orbitals [or, at least, an approximate $\pi - \sigma(\bar{\pi})$ separation as in C-phenylketenimines] is no longer possible. All the orbitals (which have no nodal planes) or excited states, respectively, of C_2 carbodi-imides transform according to the irreproducible representations a or b.

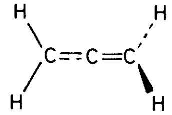
The interpretations of the u.v. spectra of the carbodi-imides (4), (6), and (8) may be based advantageously on comparisons with the isoelectronic 1,3-dimethylallene (18) and 1,3-diphenylallene (19), respectively. This makes the u.v. band assignment straightforward. In particular, for dimethylcarbodi-imide (4) whose outermost occupied orbitals are accidentally degenerate[18b] and of almost the same orbital energies which are observed for the corresponding (accidentally degenerate) orbitals of (18) [9.50 eV for (4),[18b] 9.13 or 9.26 eV for (18)[10a]] very similar spectral positions may be expected for those excitations which involve the four outermost (occupied and unoccupied, respectively) a and b orbitals. The resulting ^1A and ^1B excited states of (4) then are also related to the states (A_1, A_2, B_1, B_2) resulting from 2e, 3e excitations in allene (20).[10,11b,12a]



(18)



(19)



(20)

In the gas-phase spectrum of dimethylcarbodi-imide (4)[16a] there is a maximum at 52 350 cm^{-1}, a shoulder near 47 700—48 300 cm^{-1}, and three weak peaks with a vibrational progression of *ca.* 1000 cm^{-1} at 40 584, 39 604, and 38 700 cm^{-1}. The 48 000 cm^{-1} shoulder and the three weak peaks persist in solution (in n-heptane: $\tilde{\nu}$ 38 450, 39 400, 40 450, and 48 400 cm^{-1}),[16a] *i.e.* these bands result from valence-shell transitions. Furthermore, in the solution spectrum there exists an inflection near 44 000 cm^{-1} which corresponds to another u.v. band. The 44 000 cm^{-1} band is more pronounced in the u.v. spectra of other dialkylcarbodi-imides.[16b,20]

Information about higher excited states of dialkylcarbodi-imides may be extracted from the vacuum u.v. spectrum of di-t-butylcarbodi-imide (6) (Figure 3) where intense u.v. bands are observed at 54 300 and 62 500 cm^{-1} with an inflection near 58 000 cm^{-1} (Table 1). The spectrum of (6) is diffuse; no vibrational fine structure is found. This is probably due to the high degree of alkylation and the low frequency vibrations the alkyl groups introduce as well as the expected closeness of the u.v. bands originating from almost degenerate b and a outermost orbitals in (6).[18]

From comparisons with the u.v. spectrum of 1,3-dimethylallene (18)[9,10a,e] the bands at 39 400 and 44 000 cm^{-1} in (4) are associated with $^1A(A_2)$ and $^1B(B_1)$

excited states. The band at *ca.* 48 000 cm^{-1} should then correspond to the $^1A(A_1)$ excited state.

While a 48 000 cm^{-1} band in dialkylcarbodi-imides can be assigned to a valence-shell transition, we still have to locate the Rydberg bands and the one of lowest wavenumber is likely to occur at the same spectral region as $^1A(A_1)$. Using an ionization energy I_v of 9.0 eV for the outermost *a* and *b* orbitals of (6) [18] and approximate term values [used for allene (20) [11b] or imines [19a]] of 26 000 for 3*s*, 19 000 for 3*p*, and 13 000 cm^{-1} for 3*d* rough estimates for the Rydberg bands originating with the outermost *a* and *b* orbitals are *b*(*a*), 3*s* 46 000, *b*(*a*), 3*p* 53 000, and *b*(*a*), 3*d* 59 000 cm^{-1}. As a consequence, the 48 000 cm^{-1} band of (4) is suggested to comprise the $^1A(A_1)$ state and the *b*(*a*), 3*s* Rydberg state.

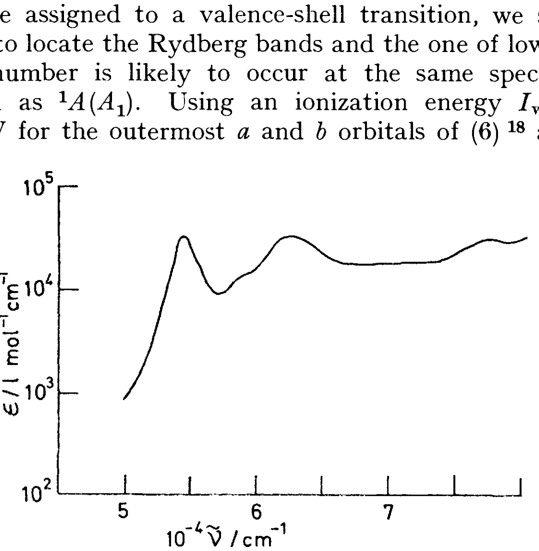
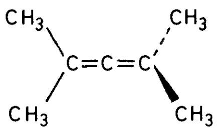
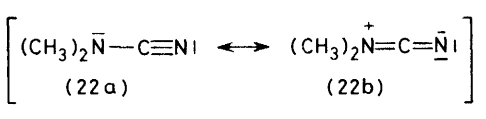


FIGURE 3 Gas-phase u.v. spectrum of di-t-butylcarbodi-imide (6)

Correspondingly, we suggest that the 54 300 cm^{-1} band of (6) is associated with two excited states, one being the *b*(*a*), 3*p* Rydberg state, the other the $^1B(B_2)$ (valence shell) state. The location of the excited state $^1B(B_2)$ of (6) at 54 300 cm^{-1} is based on the following arguments. In alkyl allenes of symmetry C_2 or D_{2d}, such as (18) or (21), the spectral position of the intense $^1B_2$ band is largely unaffected by the degree of methylation (*i.e.* also largely independent from the ionization energies of the outermost orbitals).[9,10e] Therefore, the u.v. band assignment for (21) may be used as a guideline for that of (6). Allene (21) has its $^1B_2$ band at *ca.* 58 000 cm^{-1}.[11a] Furthermore, dimethylcyanamide (22) which has a resonance form (22b) with a carbodi-imide structure exhibits a strong $^1B_2$ ($^1\Delta_u$) band (in C_{2v}) at 54 650 cm^{-1} which correlates with $^1B_2$ of allene (20) (in D_{2d}).[12a]



(21)



$$\left[(CH_3)_2\bar{N}{-}C{\equiv}N| \longleftrightarrow (CH_3)_2\overset{+}{N}{=}C{=}\overset{-}{\underline{N}}|\right]$$

(22a) (22b)

According to our previous energy considerations the 62 500 cm^{-1} band in (6) is assigned to the *b*(*a*), 3*d* Rydberg state. The shoulder at *ca.* 58 000 cm^{-1} is probably part of the Rydberg band system, as in the range 53 000—63 000 cm^{-1} four Rydberg bands should be found (*b*, 3*p*; *a*, 3*p*; *b*, 3*d*; *a*, 3*d*). The spectrum of (6), however, does not allow the differentiation of the Rydberg transitions originating from the *a* or *b* HOMO, respectively.

The assignments of the observable u.v. bands of diphenylcarbodi-imide (8) (Figure 1) present no particular difficulties. Referring to a 'molecules in molecules' approach and more or less localized excitations at the two phenyl subunits of (8) one would expect the u.v. spectrum of (8) to exhibit splittings of all the bands of the ketenimine (7) (Figure 1) or phenyl isocyanate (15), respectively, which may serve as models for a carbodi-imide with only one phenyl group. The corresponding excited states of symmetries ^1A and ^1B of (8) should then be described as symmetric or antisymmetric combinations of the (semilocalized) excitations in each of the fragments of (8). Evidently, such splittings are rather small and not observable in (8), contrary to the situation in 1,3-diphenylallene (19),[10d,e] where corresponding splittings of the electronic bands are observed in the u.v. spectrum and are even more pronounced in the c.d. spectrum.[9,10d]

A resumé of our results shows that symmetrically substituted carbodi-imides have patterns for their excited states which are very similar to those observed for the corresponding 1,3-disubstituted allenes, in particular with respect to the excited state energies. In this regard carbodi-imides (with two nitrogen atoms) are more similar to allenes than ketenimines which differ from allenes by the replacement of only one carbon atom of the C=C=C skeleton by nitrogen.

(2) *Quantum Chemical Calculations.*—As indicated in the preceding section discussion of the electronic structures of ketenimines (and carbodi-imides) in terms of concepts which are common for unsaturated molecules with heteroatoms, such as π and σ orbitals, conjugation, electron lone-pairs, *etc.*, may meet difficulties which cannot be resolved by referring only to experimental (spectroscopic) methods. Therefore, quantum chemical calculations serve as additional, valuable guidelines to inquire in more detail into the nature of the electronic structures and excited states, respectively, of the aza-cumulenes. Of the myriad of semiempirical approaches for the treatment of medium to large molecules the CNDO/S scheme has proven to be well suited for investigating both electronic ground and excited state properties.[3]

(i) *Molecular orbitals and their energies.* In Table 2 CNDO/S energies (ε_i) for the orbitals *i* of some selected ketenimines and carbodi-imides (3), (4), (9), and (13) are summarized. These orbital energies may be correlated with p.e. spectroscopically-determined vertical ionization energies *via* Koopmans' approximation [$-\varepsilon_i = I_v(i)$]. The ionization energies of the above molecules are also given in Table 2. In general, there is a satisfying numerical agreement between CNDO/S orbital energies and experimental ionization energies, which is illustrated by correlation (1) (linear correlation coefficient r 0.963 5). Therefore, CNDO/S comput-

$$I_v(i) = -0.81\ \varepsilon_i(\text{CNDO/S}) + 1.21\ (\text{in eV}) \qquad (1)$$

ations may be used to predict ionization energies of azacumulenes for which no p.e. spectra are available.

From correlation (1) the ionization energies of the (accidentally degenerate) outermost a and b orbitals of diphenylcarbodi-imide (8) have been deduced: $-\varepsilon(b)$ 8.97, $I_v(b)$ 8.46, $-\varepsilon(a)$ 9.00, $I_v(a)$ 8.50 eV. This means, that like (4) and (18) the corresponding carbodi-imide (8) and the allene (19) have very similar ionization energies. Furthermore, correlation (1) has been used to deduce the ionization energies of ketenimine (1) and carbodi-imide (2) from their CNDO/S orbital energies [I_v 8.98, 10.85, 12.91 eV for (1); I_v 10.06, 10.14, 13.06, 13.81 eV for (2)]. These last values will be used for the construction of the orbital diagrams given in Figure 4.

TABLE 2

Comparisons between ionization energies (I_v) and CNDO/S orbital energies (ε_i) of ketenimines and carbodi-imides

Compound	MO[a]	$-\epsilon_i$/ eV	$I_v(i)$/ eV	Ref.
(4)	$\left.\begin{matrix} b \\ a \end{matrix}\right\}$ $(n_N - CN)_y$	10.09	9.50	18b
	$\mp(n_N - CN)_z$	10.18		
	$\left.\begin{matrix} b \\ a \end{matrix}\right\}$ $(n_N + CN)_y$	12.71	11.55	
	$\mp(n_N + CN)_z$	13.49	12.26	
(3)[b]	$\bar{\pi}_{(1)}(a') \sim n_N - (C{=}C)_z$	8.86	7.85	17
	$\pi_{(1)}(a'') \sim (C{=}N)_y - (CX_2)_y$[c]	10.52	10.11	
	$\bar{\pi}_{(2)}(a') \sim n_N + (C{=}C)_z$	12.43	10.5	
(9)	$\bar{\pi}_{(1)}(a') \sim \bar{\pi}_{(1)}(a')$ (3)	8.88	8.02	17
	$\pi_{(1)}(a'') \sim \pi(b_1) - (C{=}N)_y$	8.89	8.88	
	$\pi_{(2)}(a'') \sim \pi(a_2)$	9.72	9.35	
(13)	$\pi_{(1)} \sim \pi(b_1) - \bar{\pi}_{(1)}(a')$ (3)	8.42	7.79	17
	$\pi_{(2)} \sim \pi(a_2)$	9.71	9.12	
	$\pi_{(3)} \sim \pi(b_1) + \bar{\pi}_{(1)}(a')$ (3)	10.85	9.91	

[a] The MOs are approximately described in terms of a LCMO scheme (see text and Figure 4). [b] Experimental values of $(CH_3)_2C{=}C{=}NC_6H_{11}$. [c] (CX_2) is a group orbital comprising essentially the $={\rm C}\!<\!{}^{\rm C}_{\rm C}$ system giving rise to CC_2 hyperconjugation.

In particular, our results demonstrate that the energies of the outermost three orbitals of (1) are not intermediate between the energies of the corresponding orbitals of allene (20) and keten ($H_2C{=}C{=}O$)[3] as deduced from *ab initio* calculations with 'floating spherical Gaussian orbitals'.[21]

In discussing the shape of the MOs of the azacumulenes our tool is (qualitative) perturbation theory starting from semilocalized group orbitals (linear combination of molecular orbitals, LCMO). In this approach the extent of mixing the different orbitals is roughly proportional to the overlap of the neighbouring basis functions of the group orbitals and inversely proportional to the energy gap between them. For ketenimine (1) the initial 'unperturbed' group (valence-bond) functions correspond to the nitrogen lone-pair n_N of energy -10.5 eV [19b] (which may be described as a sp_xp_y hybrid), the $(C{=}N)_y$ and $(C{=}C)_z$ 'double bonds' (of energies -12.4 and -10.5 eV, respectively)[19b] and a $\sigma(CH_2)$ group orbital transforming as p_y $\{C(2p)_y + [H(1s) - H'(1s)]$; ε *ca.* -13.5 eV$\}$.

The symmetric or antisymmetric combinations, respectively, of n_N with $(C{=}C)_z$ then give the a' orbitals $\bar{\pi}_{(2)}$ and $\bar{\pi}_{(1)}$ of (1). The outermost a'' (π) system of (1) comprises essentially the $(C{=}N)_y$ double bond which interacts mesomerically with the CH_2 group orbital ('hyperconjugation') (Figure 4). A qualitatively similar situation is found in trimethylketenimine (3).

The interaction between n_N and $(C{=}C)_z$ is so efficient that the resulting orbital $[\bar{\pi}_{(1)}(a')]$ may no longer be viewed as a 'one-centre' orbital (lone-pair), but rather a three-centre group orbital. On the other hand, the lowest energy virtual orbitals are practically $(C{=}C)_z$ or $(C{=}N)_y$ two-centre orbitals.

According to the CNDO/S calculations $\bar{\pi}_{(1)}$ (a') [of (1) and (3)] is calculated as having 20—25% nitrogen character. This indicates that in ketenimines the nitrogen character of the HOMO has decreased by about one-half when compared with the situation in imines[19b] and that in ketenimines the HOMO $\bar{\pi}_{(1)}$ has lost its 'lone-pair' character.

In a corresponding schematic diagram (Figure 4) the orbitals of carbodi-imides may be constructed by interactions of the two nitrogen lone-pairs n_N with corresponding π-type C=N orbitals. Owing to the larger energy gap between n_N and C=N (than between n_N and C=C) the outermost (b and a) occupied orbitals of carbodi-imide (2) resemble more (appropriate combinations of) lone-pairs than the $\bar{\pi}_{(1)}$ (a') orbital in ketenimines. In the schematic diagram in Figure 4 n_N and C=N first combine to give degenerate $(n_N \mp CN)_y$ and $(n_N \mp CN)_z$ MOs (of energies 10.10 and 13.45 eV, respectively) which then *via 'secondary'* interactions split into the symmetry adapted b and a orbitals $[(n_N \mp CN)_y \mp (n_N \mp CN)_z]$. In order to avoid confusion these last orbitals are not displayed in Figure 4.

On the other hand, the lowest energy unoccupied orbitals of carbodi-imides are best described as symmetric or antisymmetric combinations of π-type virtual $(C{=}N)_y$ and $(C{=}N)_z$ orbitals.

Substituting a hydrogen at the nitrogen atom by a phenyl group [(1) $\longrightarrow$ (14)] leaves the $\bar{\pi}(a')$ system of (1) (of energy *ca.* 8 eV) almost unchanged, whereas the $\pi(a'')$ ketenimine orbital (of energy *ca.* 10.5 eV) may interact (*via* nitrogen) with the $\pi(b_1)$ component of the originally degenerate $1e_{1g}$ orbital of benzene $[-\varepsilon(1e_{1g})$ 9.25 eV$]$.[10a] As usual, the $\pi(a_2)$ component of the benzene $1e_{1g}$ orbital remains largely unaffected in (14). Corresponding arguments also apply if one compares the methylated ketenimines (3) and (9). All these last molecules have a strict $\pi(a'') - \sigma(a')$ separation of their MOs.

In the *C*-phenylketenimine (13) the $\pi(b_1)$ orbital of the phenyl ring may interact through π-type overlap *via* carbon with the $\bar{\pi}_{(1)}(a')$ C=C=N orbital to give $\pi_{(1)}$ and $\pi_{(3)}$ in (13). Owing to the relatively large energy gap (*ca.* 1.2 eV) between $\pi(b_1)$ and $\bar{\pi}_{(1)}(a')$ the HOMO in (13) is expected to retain considerably more of its ketenimine character than in the *N*-phenylketenimine (9). The CNDO/S calculations indicate 50% C=C=N character in (13) *versus* 20% in (9). As the molecule (13) lacks any symmetry the $\pi - \sigma$ separability of the MOs should break down. Inspection of the CNDO/S LCAO expansions for the outermost orbitals of (13), however, confirm that there is very little mixing of the $\pi_{(1)}$ orbitals [$\pi_{(i)} \sim \pi(b_1) \mp \bar{\pi}_{(1)}(a')$] with other orbitals. The same holds for $\pi_{(2)} \sim \pi(a_2)$. Therefore, the CNDO/S calculations justify the assumption that, with respect to their nodal properties, these last orbitals may be regarded as ' π orbitals '.

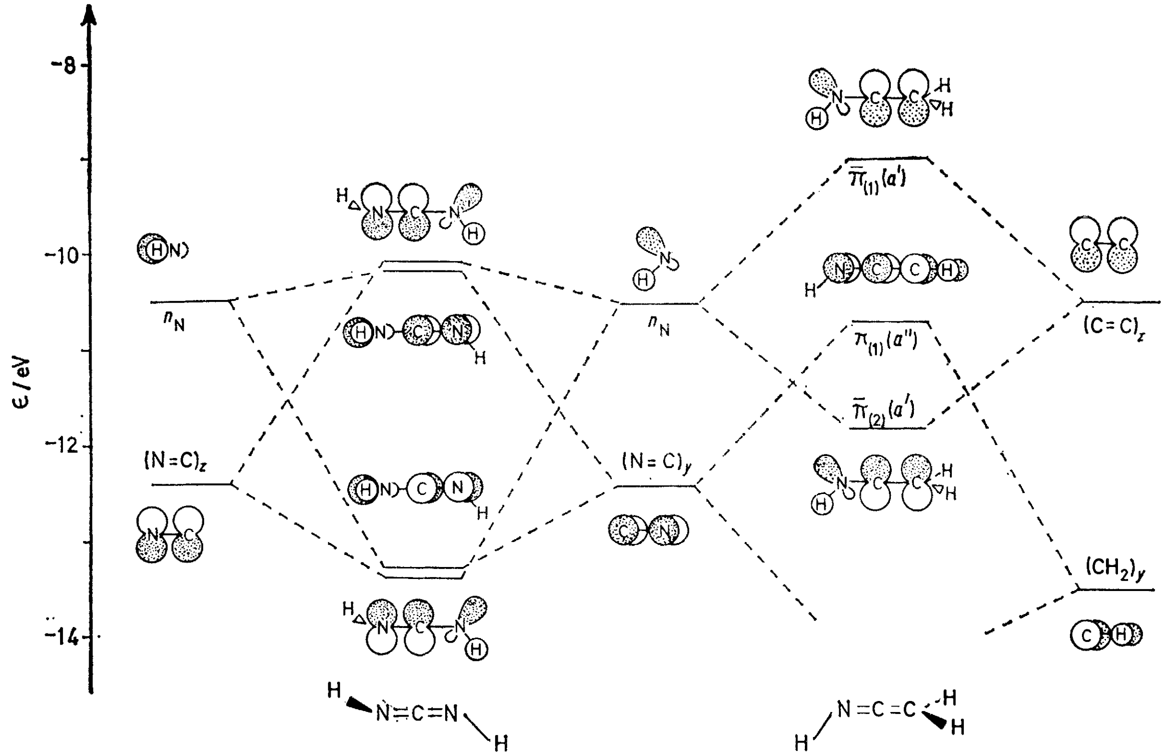


Figure 4 Schematic orbital interaction diagram for ketenimine and carbodi-imide (secondary interactions which lift the degeneracies of the carbodi-imide orbitals are not given)

In diphenylcarbodi-imide (8) the outermost (occupied and unoccupied) orbitals are largely combinations of benzene π-type orbitals (as in *N*-phenylketenimines), *i.e.* most of the electron density is located at the phenyl rings.

(ii) *Excited states.* In Table **3** calculated and (for immediate comparison) observed excited states energies and intensities of the corresponding electronic bands of some ketenimines and carbodi-imides are given. In most cases the computations predict more excited states to exist in the spectral range under consideration than are found experimentally. This means that the quantum chemical calculations aid in ' resolving ' experimentally observed spectral bands.

The theoretical values for the lowest energy transitions of the trialkylketenimines (3) and (5) and dialkylcarbodi-imides (4) and (6) deviate considerably from the experimental ones (by 0.6—1.2 eV). This, however, is due to an inherent deficiency of the CNDO/S scheme and is always observed for transitions involving perpendicular *p* orbitals (as in the CNDO/S scheme exchange integrals involving p_y and p_z AOs are neglected). Furthermore, the CNDO/S scheme calculates the lowest energy excited states of (4) to be accidentally degenerate, in disagreement with the experimental results. On the other hand, for the (larger) phenyl derivatives the u.v. spectra are almost quantitatively reproduced by the CNDO/S calculations.

From the computational results in Table **3** it is seen that the ${}^1A''$ excited states in trialkylketenimines (3) and (5) may be described by single electronic configurations, whereas the lowest energy ${}^1A'$ excited state is a mixture of configurations [essentially a mixture of $(\bar{\pi}_{(1)}, \bar{\pi}_{(-1)})$ and $(\bar{\pi}_{(1)}, \bar{\pi}_{(-2)})$]. On the other hand, the CI composition of the excited states of *N*-phenyl(dimethyl)ketenimine (9) reveals that, within the CNDO/S scheme, no excited state of *N*-phenylketenimines can be described by a single electronic configuration. The lowest energy ${}^1A''(\bar{\pi}, \pi^*)$ excited state is a mixture of two $\bar{\pi},\pi^*$ configurations. As is observed in phenylallenes[10a,d] the B_{1u}, $E_{1u(a)}$ and $E_{1u(b)}$ states do not result only from π,π^* transitions, but contain admixtures of σ, σ^* excitations [$\bar{\pi}_{(1)}$, $\bar{\pi}_{(-1)}$].

The CNDO/S calculations of (9) predict the existence

TABLE 3

Theoretical (CNDO/S) and experimental excited states energies and intensities of electronic transitions of ketenimines and carbodi-imides

Excited state	Experimental		Theoretical		
	ΔE/eV	f [a]	ΔE/eV	f	CI composition [b]
N-s-Butyl(ethyl)(methyl)ketenimine (5) [HOMO: $\bar{\pi}_{(1)}$ (17); LUMO: $\bar{\pi}_{(-1)}$ (18)] [c]					
$^1A''(\bar{\pi},\pi^*)$	4.25	1×10^{-3}	3.68	3×10^{-5}	−0.99 (17, 19)
$^1A''(\pi,\bar{\pi}^*)$	5.16	0.010	5.15	4×10^{-5}	−1.00 (16, 18)
$^1A'(\bar{\pi},\bar{\pi}^*)$	6.04	0.065	6.12	0.46	0.80 (17, 18) + 0.51 (17, 20)
N-Phenyl(ethyl)(methyl)ketenimine (10) [HOMO: $\bar{\pi}_{(1)}$ (28); LUMO: $\pi_{(-1)}$ (29)] [d]					
$^1A''(\bar{\pi},\pi^*)$	3.72	2×10^{-3}	3.51	2×10^{-5}	0.68 (28, 29) + 0.70 (28, 32)
$^1A'(B_{2u})$	4.38	6×10^{-3}	4.43	0.012	−0.79 (27, 30) + 0.59 (26, 29)
$^1A''(\pi,\bar{\pi}^*)$			4.81	1×10^{-5}	0.91 (27,31) −0.42 (24,31)
$^1A'(B_{1u})$	5.33	0.12	5.05	0.85	0.91 (27, 29) −0.38 (28, 31)
$^1A''(\bar{\pi},\pi^*)$			5.55	0.0	0.46 (28, 29) −0.38 (28, 32) +0.66 (28, 30) +0.30 (28, 33)
$^1A''(\bar{\pi},\pi^*)$			5.62	0.0	0.49 (28, 29) −0.38 (28, 32) −0.67 (28, 30) +0.30 (28, 33)
$^1A'(E_{1u(a)})$	5.95	0.10 [e]	6.11	0.61	−0.74 (26, 30) +0.30 (27, 32) −0.55 (28, 31)
$^1A'(E_{1u(b)})$	6.20	0.23	6.34	0.87	−0.58 (27, 30) −0.73 (26, 29) −0.28 (28, 31)
N-s-Butyl(methyl)(phenyl)ketenimine (12) [HOMO: $\pi_{(1)}$ (28); LUMO: $\pi_{(-1)}$ (29)] [f]					
$^1A''(\pi,\bar{\pi}^*)$	3.59	4×10^{-3}	3.25	2×10^{-4}	0.87 (28, 31) −0.33 (26, 31) −0.32 (28, 32)
$^1A'(B_{2u})$	4.38	6×10^{-3} [g]	4.28	6×10^{-3}	−0.79 (28, 30) −0.51 (27, 29) −0.25 (26, 30)
$^1A'(B_{1u})$	4.49	0.26	4.48	0.35	−0.98 (28, 29)
$^1A''(\bar{\pi},\pi^*)$			4.87	2×10^{-3}	0.81 (25, 29) +0.52 (25, 32)
$^1A'(E_{1u(a)})$	5.37	0.09	5.74	0.056	0.52 (28, 30) −0.61 (27, 29) −0.42 (28, 32) −0.34 (26, 30)
			5.86	0.19	−0.31 (28, 31) −0.27 (28, 30) +0.26 (27, 29) −0.74 (28, 32)
$^1A'(E_{1u(b)})$	6.20	0.13	6.13	0.060	0.72 (27, 30) −0.62 (26, 29)
			6.53	0.050	0.26 (27, 29) −0.28 (26, 30) +0.72 (23, 30) −0.52 (25, 30)
Dimethylcarbodi-imide (4) [h] [HOMO: *b* (14); LUMO: *a* (15)]					
$^1A(A_2)$	4.88	2×10^{-3}	4.11	4×10^{-5}	0.78 (14, 16) +0.61 (13, 15)
$^1B(B_1)$	5.45	0.01	4.12	5×10^{-5}	−0.72 (14, 15) −0.68 (13, 16)
$^1A(A_1)$	6.00		5.32	4×10^{-4}	−0.57 (14, 16) +0.76 (13, 15) −0.28 (12, 16)
^1B			6.79	3×10^{-3}	0.94 (12, 15) −0.30 (11, 16)
^1A			7.07	6×10^{-5}	0.74 (12, 16) −0.65 (11, 15)
$^1B(B_2)$	6.73	0.26	7.34	0.86	−0.51 (14, 15) +0.54 (13, 16) +0.50 (11, 16) +0.30 (14, 16)
Diphenylcarbodi-imide (8) [HOMO: *b* (36); LUMO: *a* (37)]					
^1B	3.90	1×10^{-3}	4.24	2×10^{-3}	−0.61 (36, 37) −0.54 (35, 38) −0.33 (36, 41) −0.31 (35, 42)
^1A			4.24	2×10^{-4}	−0.61 (36, 38) −0.55 (35, 37) −0.34 (36, 42) −0.30 (35, 41)
$^1B(B_{2u})$	4.38	0.070	4.47	4×10^{-3}	−0.52 (36, 39) −0.55 (35, 40) +0.42 (34, 37) −0.42 (35, 38)
$^1A(B_{2u})$			4.47	2×10^{-3}	−0.52 (36, 40) −0.55 (35, 39) +0.42 (33, 37) −0.42 (34, 38)
$^1B(B_{1u})$	5.12	0.25	4.76	1.11	−0.67 (36, 37) +0.73 (35, 38)
$^1A(B_{1u})$			5.11	0.13	0.61 (36, 38) −0.69 (35, 37)
$^1A(E_{1u(a)})$	6.20	0.56	5.85	8×10^{-4}	−0.35 (34, 40) −0.35 (33, 39) −0.52 (36, 42) +0.54 (35, 41) +0.30 (32, 38)
$^1B(E_{1u(a)})$			6.14	0.26	−0.42 (36, 39) −0.48 (34, 39) −0.49 (33, 40), +0.38 (36, 41) −0.33 (35, 42)
$^1B(E_{1u(b)})$			6.17	0.37	−0.71 (36, 39) +0.47 (35, 40) +0.29 (34, 39) +0.26 (33, 40)
$^1A(E_{1u(b)})$			6.17	0.012	−0.81 (36, 40) +0.49 (35, 39) +0.25 (32, 40)

[a] Estimated oscillator strengths. [b] Only configurations with CI coefficients greater than 0.25 are given. [c] Theoretical values are for (3). [d] Theoretical values are for (9) which has practically the same u.v. spectrum as (10).[15b] [e] Only observable for (7). [f] Theoretical values are for (11). [g] Not observable, see text. [h] Bands with $\Delta E > 6.00$ eV are from the gas-phase spectrum of (6).

of three further $^1A''$ (π, $\bar{\pi}^*$) excited states in the energy region $\tilde{\nu} \leqslant 50\,000$ cm^{-1} which cannot be observed experimentally. By analogy with (3) the existence of only one $^1A''$ excited state (of energy *ca.* 5.0 eV) involving essentially the ($\pi_{(1)}$, $\bar{\pi}_{(-1)}$) configuration would be expected.

The CNDO/S results for the *C*-phenylketenimine (11) which may be compared with the experimental ones of (12) corroborate our assumption that the 'B_{2u} band' is buried by the strong 'B_{1u} band'. Furthermore, the calculations predict the existence of a second low energy $^1A''$ excited state near 4.8 eV and indicate that in *C*-phenylketenimines each of the $E_{1u(a)}$ and $E_{1u(b)}$ bands should be associated with two excited states involving corresponding electronic configurations.

Concerning α-substitution of a *C*-phenylketenimine [(13) $\longrightarrow$ (11)] the CNDO/S scheme calculates a bathochromic shift of the $^1A'(B_{1u})$ band by *ca.* 450 cm^{-1} [$\tilde{\nu}$(CNDO/S) 36 595 cm^{-1} for (13), $\tilde{\nu}$(CNDO/S) 36 147 cm^{-1} for (11)]. This would be similar to the situation observed for the phenylallenes (16) and (17), but contrary to the situation for styrenes [$C_6H_5CH{=}CH_2$, $C_6H_5(CH_3)C{=}CH_2$] where one observes a hyposochromic shift of the corresponding band. If one compares the spectral positions of $C_6H_5CH{=}C{=}NCH(CH_3)_2$ ($\tilde{\nu}$ 37 000 cm^{-1})[22] and (12) ($\tilde{\nu}$ 36 250 cm^{-1}, Table 1) the bathochromic shift of corresponding magnitude is indeed found experimentally. That means, the CNDO/S scheme is able to reproduce small substituent effects in the series of phenyl derivatives. For the dialkylcarbodi-imides (4) and (6), on the other hand, the agreements between calculated and observed excited states energies (resulting from valence shell transitions) are rather bad. Only the position of the high energy intense $^1B(B_2)$ band is calculated satisfactorily by the CNDO/S scheme. However, the calculations (which predict two further weak bands) give the correct energy sequence of the excited states.

In the case of diphenylcarbodi-imide (8) the observable bands are reproduced satisfactorily by the CNDO/S calculations. Furthermore, the CNDO/S results corroborate our anticipation that the excited states of (8) exhibit pairwise accidental degeneracies. Splittings are only predicted for the $^1B_{1u}$ and $^1E_{1u(a)}$ bands. Obviously, the CNDO/S scheme overestimates the splittings of these last excited states, as a gap of *ca.* 0.3 eV should be observable in the u.v. spectrum of (8). For instance, the splitting of the corresponding $^1B(B_{1u})$ and $^1A(B_{1u})$ bands in 1,3-diphenylallene (19) amounts to 3 700 cm^{-1} (0.46 eV).[9,10d]

Our results concerning excited states and electronic structures of azacumulenes allow a qualitative discussion of their ^{15}N n.m.r. shifts. In ref. 8 Roberts has suggested that the ^{15}N chemical shifts of carbodi-imides in comparison to those of imines result essentially from the paramagnetic shielding term *via* different excitation energies ΔE of the lowest energy magnetic allowed transitions in both kinds of molecules (a reduction in ΔE increasing the contribution to the paramagnetic shielding). Our results do not support this particular view though we agree that it is largely the paramagnetic shielding constant which governs the difference in the ^{15}N chemical shifts of carbodi-imides and imines. Alkylated carbodi-imides and imines, such as (4) and $(CH_3)_2CHCH{=}NC_2H_5$, have comparable HOMO $\longrightarrow$ LUMO transition energies [39 400 cm^{-1} (Table 1) *versus* 41 000 cm^{-1}[19a]]. However, as for constant excitation energies a decrease of the LCAO coefficients decreases the contribution of the paramagnetic shielding,[3,23] the considerably reduced nitrogen lone-pair character in carbodi-imides relative to that in imines should be mainly responsible for the observed differences in ^{15}N chemical shifts of both these nitrogen systems. The different 'lone-pair' character of the orbitals in carbodi-imides and imines is also qualitatively observable in the different behaviour of the ^{15}N resonances when changing a neutral solvent into one capable of hydrogen bonding.

(iii) *Electron density distributions.* A central concept in chemistry (and also spectroscopy) is the electron density associated with a particular atom of a molecule. As the quantum-chemically determined electron densities (as a set of indices characterizing the electron density distribution of a molecule) depend upon the definition adopted (electron density, gross atomic population, *etc.*)[3,24b] and upon the basis set underlying the particular calculations, useful information can only be extracted from such indices if one compares the electron densities of a larger set of related molecules. In this contribution we present CNDO/S total electron densities of nine prototypical ketenimines and carbodi-imides (including CO_2) (Figure 5), which hence allow comparisons with the (CNDO/S) electron density distributions in other triatomic cumulenes (allenes,[3,10a,24] ketens,[3,24] diazo-compounds[3,24]). Our reported electron densities are comparable with those obtained on an *ab initio* level, as the CNDO/S electron densities correlate with *ab initio* STO-3G gross atomic populations.[3,24b]

As expected from electronegativity considerations the electron densities $P_{CC}(2')$ of the central atoms of the parent azacumulenes (1) and (2) are markedly reduced when substituting a terminal carbon atom of the allene moiety by nitrogen. Isoelectronic substitution of one CH unit by N [(20) $\longrightarrow$ (1) $\longrightarrow$ (2)] reduces $P_{CC}(2')$ by *ca.* 0.120 e.

A difference of *ca.* 0.240 e is also observed if one compares the central atom electron densities $P_{CC}(2')$ of the substituted carbodi-imides (4) and (8) and allenes (18)[3,10a] and (19).[3]

Concerning $P_{CC}(2')$ carbodi-imide (2) takes strictly an intermediate position between allene (20) and carbon dioxide (23) (Figure 5) according to equation (2) (*r* $-0.990\,9$) which relates $P_{CC}(2')$ to the nuclear charge *Z*

$$P_{CC}(2')(\text{CNDO/S}) = 3.934 - 0.225\,(Z - 6) \qquad (2)$$

of the terminal heavy atoms (C, N, O) of the corresponding cumulene skeletons. The substitution of a hydrogen at the nitrogen atom by a methyl or phenyl group [(1) ⟶ (14), (2) ⟶ (4), (2) ⟶ (8)] is accompanied by a reduction of the strong negative charge at the nitrogen atom. The substituent effects of the methyl and phenyl groups when linked to carbon on the electron densities of C-1′ and -2′ are similar to those observed in case of allenes.[3]

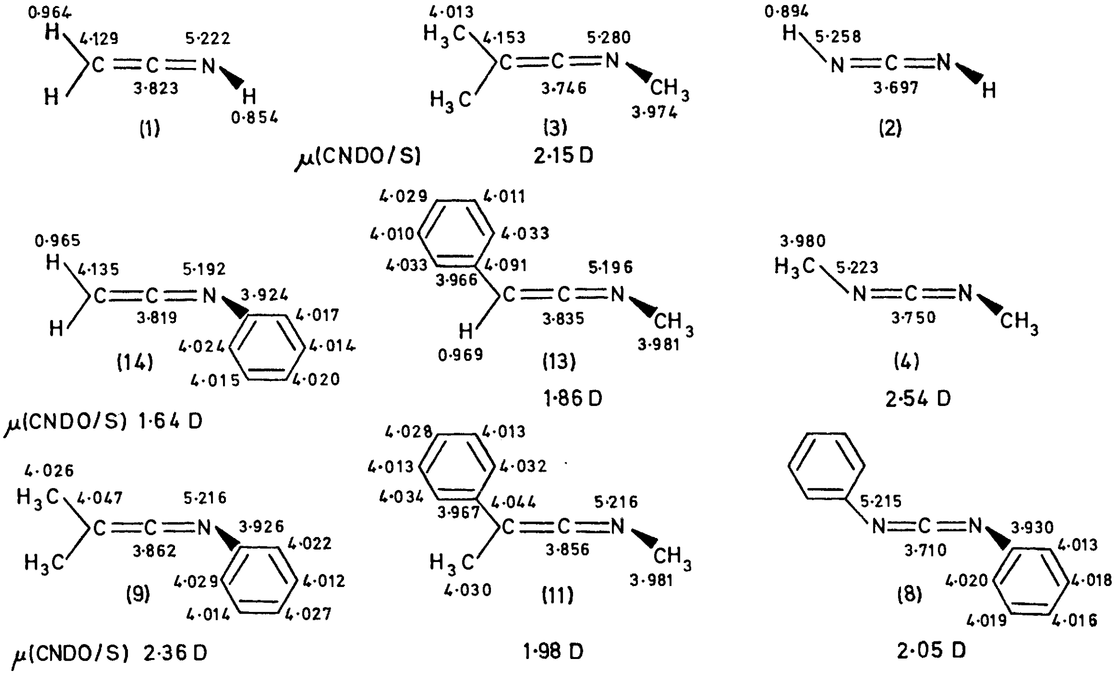


FIGURE 5 CNDO/S total electron densities and dipole moments of ketenimines and carbodi-imides [for comparison $P_{CC}(1')$ 4.099 e and $P_{CC}(2')$ 3.940 e for allene (20),[3,10a] $P_{OO}(1')$ 6.255 e and $P_{CC}(2')$ 3.491 e for carbon dioxide]

If one views the overall charge densities $\Sigma\rho_{CC} = \Sigma(P_{CC} - 4.000)$ of the phenyl group carbon atoms in (14), (9), and (11) (Table 4) as a measure of the electron-donating ability of the CCN unit, one may conclude that (a) the ketenimine functionality acts as a donor irrespective of whether the particular group is bonded *via* carbon or nitrogen and (b) that the electron-donating ability increases in the series $H_2C{=}C{=}N < (CH_3)_2C{=}C{=}N < CH_3C{=}C{=}NCH_3$. This means that electron density transfer is easier *via* the terminal carbon atom than *via* the nitrogen atom and the more pronounced flow of electron density is opposite to the direction of the electric dipole moment of the molecules. Taking the ^{13}C chemical shifts δ_{C_p} of the *para*-carbon atoms of the corresponding phenylketenimines[6] as an experimental measure of the donor character of a group,[6c] one observes a direct relationship between $\Sigma\rho_{CC}$ and δ_{C_p}.

TABLE 4

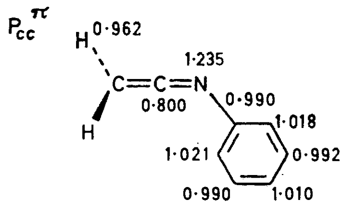
Overall charge densities ($\Sigma\rho_{CC}$) of the phenyl groups in ketenimines and ^{13}C *para*-carbon atom resonances [a]

Compound	$\Sigma\rho_{CC}$	Compound	δ_{C_p} (p.p.m.)
(14)	−0.014	(14)	127.12
(9)	−0.030	(10)	126.50
(11)	−0.087	(12)	124.97

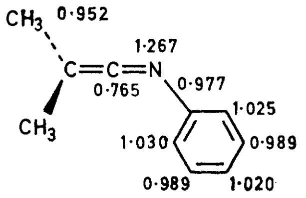
[a] From ref. 6.

The overall charge density of diphenylcarbodi-imide (8) ($\Sigma\rho_{CC}$ − 0.016 e) demonstrates that also the NCN entity acts as a donor group as has been deduced by Roberts[8] from ^{13}C resonances.

A closer inspection of the π electron densities P^{π}_{CC} of the *N*-phenylketenimines (9) and (14) reveals that the charge transfer from the CCN group into the phenyl ring results largely from a π electron redistribution and that in transferring π electron density CC_2 hyperconjugation (9) is more effective than CH_2 hyperconjugation (14).



(14)



(9)

An observable directly related to the electron density distribution of a molecule is its dipole moment (μ). Substituted ketenimines and carbodi-imides have calculated dipole moments [μ(CNDO/S)] in the range 1.6—2.5 D (Figure 5). Comparisons between calculated and experimental dipole moments are only possible for the carbodi-imides (4) and (8). In these cases the agreements are satisfying [μ 1.70 D for (8) [25a] and μ 2.08 D for $(CH_3)_2CHN=C=NCH(CH_3)_2$ [25b] which may be compared with (4) as the different alkyl groups exhibit almost the same effects]. Therefore, all the theoretical values seem to give reasonable estimates for the dipole moments of the ketenimines.

We thank Dr. J. Kroner, München, Germany, for making possible the publication of the u.v. spectrum of (6) and Professor J. C. Jochims, Konstanz, Germany, for providing us with the u.v. spectrum of (8). Furthermore, we gratefully acknowledge permission by Professor A. Dondoni, Ferrara, Italy, to use his p.e. spectra of ketenimines prior to their publication. We thank the Leibniz Rechenzentrum der Bayerischen Akademie der Wissenschaften, München, for computer time.

[0/532 *Received*, 9*th April*, 1980]

REFERENCES

[1] (*a*) G. R. Krow, *Angew. Chem.*, 1971, **83**, 455; (*b*) F. Kutzer and K. Douraghi-Zadeh, *Chem. Rev.*, 1967, **67**, 107.

[2] S. Patai, ' The Chemistry of Ketenes, Allenes and Related Compounds,' Wiley, Chichester, 1980.

[3] W. Runge, *Progr. Phys. Org. Chem.*, in the press.

[4] J. R. Reilly, G. R. Krow, and K. C. Ramey, *J. Org. Chem.*, 1972, **37**, 2364.

[5] (*a*) J. C. Jochims and F. A. L. Anet, *J. Amer. Chem. Soc.*, 1970, **92**, 5524; (*b*) F. A. L. Anet, J. C. Jochims, and C. H. Bradley, *ibid.*, p. 2557; (*c*) J. C. Jochims, S. Herzberger, B. Gambke, and F. A. L. Anet, *Tetrahedron Letters*, 1977, 2255.

[6] (*a*) J. Firl, W. Runge, W. Hartmann, and H.-P. Utikal, *Chem. Letters*, 1975, 51; (*b*) W. Runge, *Org. Magnetic Resonance*, 1980, **14**, 25.

[7] F. A. L. Anet and I. Yavari, *Org. Magnetic Resonance*, 1976, **8**, 327.

[8] I. Yavari and J. D. Roberts, *J. Org. Chem.*, 1978, **43**, 4689.

[9] W. Runge in ref. 2, ch. 3.

[10] (*a*) W. Runge, W. Kosbahn, and J. Kroner, *Ber. Bunsengesellschaft Phys. Chem.*, 1975, **79**, 371; (*b*) W. Runge and J. Winkler, *ibid.*, p. 610; (*c*) J. Kroner, W. Kosbahn, and W. Runge, *ibid.*, 1977, **81**, 826; (*d*) W. Runge and P. Vermeer, in preparation; (*e*) W. Runge in ' The Chemistry of Allenes,' ed. S. R. Landor, Academic Press, London, ch. 10.

[11] (*a*) J. D. Scott and B. R. Russell, *J. Amer. Chem. Soc.*, 1973, **95**, 1429; (*b*) K. Fuke and O. Schepp, *Chem. Phys.*, 1979, **38**, 211.

[12] (*a*) J. W. Rabalais, J. M. McDonald, V. Scherr, and S. P. McGlynn, *Chem. Rev.*, 1971, **71**, 73; (*b*) J. W. Rabalais, J. M. McDonald, and S. P. McGlynn, *J. Chem. Phys.*, 1969, **51**, 5103; (*c*) K. Wittel, J. L. Meeks, and S. P. McGlynn in ' The Chemistry of Cyanates and Their Thio Derivatives,' ed. S. Patai, Wiley, Chichester, 1977, ch. 1.

[13] W. Runge in ref. 2, ch. 2.

[14] J. B. Moffat, *J. Mol. Structure*, 1979, **52**, 275.

[15] (*a*) L. A. Singer and G. A. Davis, *J. Amer. Chem. Soc.*, 1967, **89**, 598; (*b*) L. A. Singer and G. A. Davis, ' DMS UV Atlas of Organic Compounds,' Butterworths, London and Verlag Chemie, Weinheim, 1966, vol. II.

[16] (*a*) G. Rapi and G. Sbrana, *J. Amer. Chem. Soc.*, 1971, **93**, 5213; (*b*) A. Franssen, *Bull. Soc. chim. France*, 1928, **43**, 177; (*c*) H. Behringer and H. Meier, *Annalen*, 1957, **607**, 67.

[17] F. Bernardi, A. Bottoni, A. Battaglia, G. Distefano, and A. Dondoni, *Z. Naturforsch.*, 1980, **35a**, 521.

[18] (*a*) J. Kroner, W. Strack, F. Holsboer, and W. Kosbahn, *Z. Naturforsch.*, 1973, **28b**, 188; (*b*) A. Schouten and A. Oskam, *Inorg. Chim. Acta*, 1977, **22**, 149.

[19] (*a*) D. Vocelle, A. Dargelos, R. Pottier, and C. Sandorffy, *J. Chem. Phys.*, 1977, **66**, 2860; (*b*) J. B. Peel and G. D. Willet, *J.C.S. Faraday II*, 1976, 1799; (*c*) C. J. Seliskar, *J. Phys. Chem.*, 1977, **81**, 660; (*d*) R. Cimaraglia and J. Tomasi, *J. Amer. Chem. Soc.*, 1977, **99**, 1135.

[20] J. N. Murrell, ' The Theory of the Electronic Spectra of Organic Molecules,' Methuen, London, 1963.

[21] L. J. Weimann and R. E. Christofferson, *J. Amer. Chem. Soc.*, 1973, **95**, 2074.

[22] A. F. Hegarty and D. G. McCarthy, *J. Amer. Chem. Soc.*, 1979, **101**, 1345.

[23] K. A. K. Ebraheem and G. A. Webb, *Org. Magnetic Resonance*, 1977, **9**, 241, 248.

[24] (*a*) W. Runge and W. Kosbahn, *Ber. Bunsengesellschaft Phys. Chem.*, 1976, **80**, 1330; (*b*) W. Runge, W. Kosbahn, and J. Kroner, *ibid.*, 1977, **81**, 841.

[25] (*a*) F. Feichtmeyer and F. Würstlin, *Ber. Bunsengesellschaft Phys. Chem.*, 1963, **67**, 434; (*b*) W. C. Schneider, *J. Amer. Chem. Soc.*, 1950, **72**, 761.