QUANTUM-CHEMICAL INVESTIGATION OF SOME OLIGOMERIC HETEROAROMATIC COMPOUNDS

III.* AROMATIC IMIDES

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The results of calculations by the Pariser–Parr–Pople method and the expanded Hückel method of oligomeric compounds and fragments from which aromatic polyimide macromolecules are constructed are presented and discussed. In connection with the controversial character of the problem of the structures of the intermediates in the destruction of polyimides and the use, in this case, of the concept of imide–isoimide rearrangement, the relative advantageousness of the tautomeric forms of imides is evaluated, the participation of the imide ring in one or another form in conjugation is discussed, the spectral differences in the forms are established, etc. The strength characteristics of the bonds in polyimides were estimated in connection with the possibility of homolytic and hydrolytic cleavage of polyimides at these bonds.

The present communication contains the results of an investigation, within the framework of the Pariser–Parr–Pople (PPP) method and the extended Hückel method (EHM), of oligomeric compounds and fragments from which aromatic polyimide macromolecules – representatives of one of the promising classes of heat-resisting polymers [2] – are constructed. Maleinimide (I), N-phenylmaleinimide (II), phthalimide (III), N-phenylphthalimide (IV), and their iso forms (Ii, IIi, IIIi, and IVi, respectively), p-phenylene-N,N'-diphthalimide (V), pyromellitimide (VI), N,N-diphenylpyromellitimide (VII) and its unsymmetrical iso form (VIIi), diphenyltetracarboxylic acid N,N'-diphenyldiimide (VIII), as well as the dimer (IX) of aromatic pyromellitimide (Figs. 1 and 2) were calculated. The methodical details of the calculations and the parameters used were reported in [3]. In addition, we note that when the variable β method [4,5] is used, the comparison of the quantum-chemical characteristics of the molecules, calculated with the so-called different "ring character," should be made quite cautiously. Our calculations demonstrated that values such as the total electron energy, the π-bond energy, and the vertical resonance energy depend considerably on the set of variation constants used. The use of the so-called mono-, bi-, or tricyclic variation constants has virtually no effect on the characteristics of the electron-density distribution and, consequently, on the dipole moments and the energies of the upper occupied and lower vacant MO. The results obtained with identical sets of variation constants should, of course, be used in the comparison.

In the calculations, all of the compounds were assumed to have planar structures; all of the rings were assumed to be regular polygons. The lengths of all of the bonds in the imide and condensed (with the imide rings) aromatic rings were 1.38 Å, while the lengths of the bonds in the uncondensed benzene rings were 1.40 Å. The exocyclic bonds were directed along the bisectors of the corresponding external angles and had the following lengths: C=O 1.22 Å, C=N 1.27 Å, =N–C 1.35 Å, and carbon–carbon bonds between the rings 1.50 Å.

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*See [1] for communication II.

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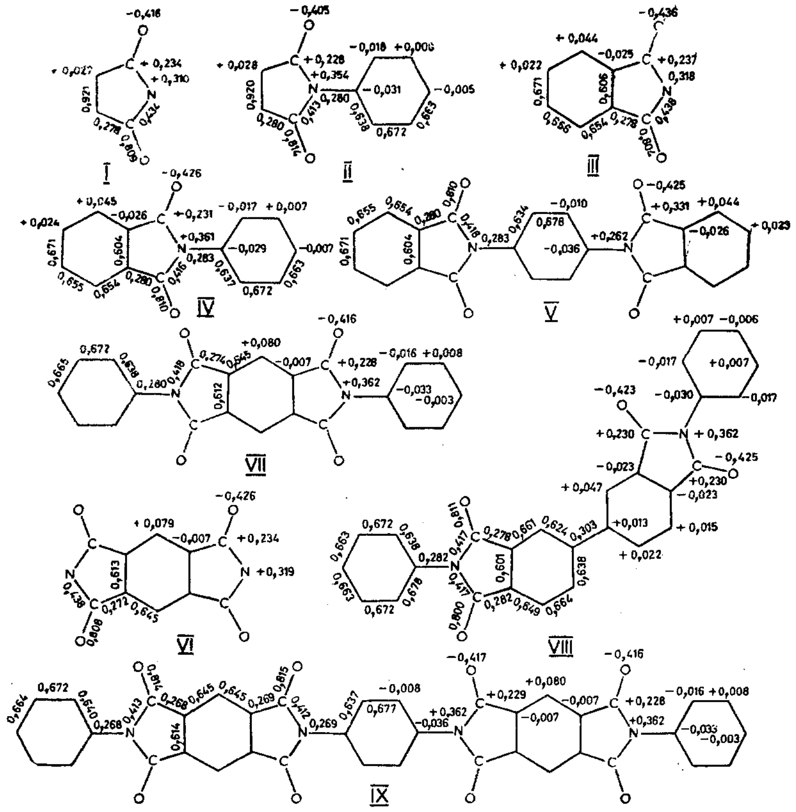

Fig. 1. Molecular diagrams of imide forms (PPP method).

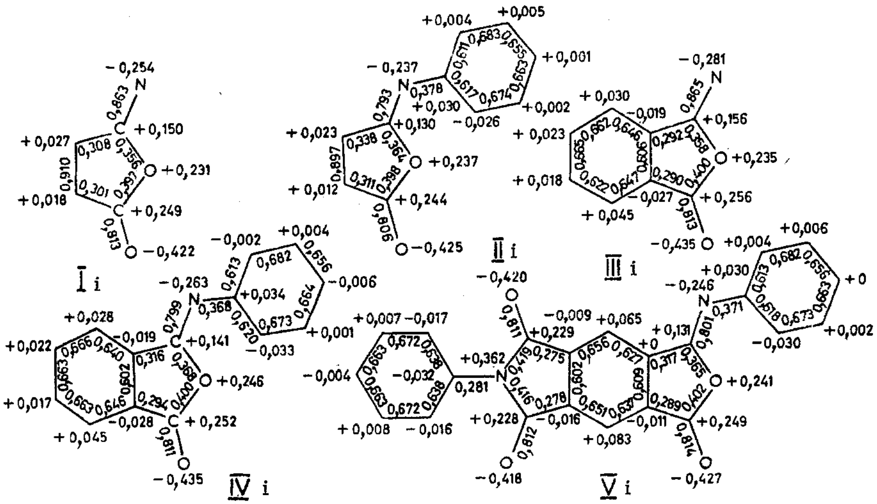

Fig. 2. Molecular diagrams of isoimide forms (PPP method).

RESULTS AND DISCUSSION

Molecular Diagrams. The distributions of the electron densities in the ground states of the investigated molecules are presented in the form of molecular diagrams in Figs. 1 and 2. A large nonuniformity in the distribution of the charges on the atoms and a considerable difference in the orders of the bonds in the imide rings are common to all of them, which may be evidence for their low aromatic character. There are $\overset{+}{N}-\overset{+}{C}$ bonds and a large excess of electron density on the oxygen atoms of the carbonyl groups in all of the imide rings.

The effect of the addition of a benzene ring to the imide ring at the N atom or of condensation (annelation) of these rings on the electron-density distribution in the imide ring can be judged from a comparison

TABLE 1. Characteristics of the Electron Transitions and Calculated Dipole Moments of the Ground (μ^{gr}) and Excited (μ_a^{ex}) States

Structure	μ^{gr}, D	λ_{max}, nm	f_{0-a}	μ_a^{ex}, D
I	0,64	300	0,01	0,73
		247	0,92	0,63
Ii	1,42	259	0,70	3,92
		247	0,34	3,78
II	1,12	370	0,03	14,62
		285	~0	18,57
IIi	1,88	359	0,95	10,68
		302	~0	11,81
III	1,95	304	0,09	5,34
		286	0,02	8,30
IIIi	2,02	288	0,11	5,14
		260	0,43	7,53
IV	2,44	333	0,01	13,95
		266	~0	19,70
IVi	2,31	355	0,86	10,60
		284	~0	14,16
VIIi	1,83	391	0,72	15,26
		361	0,20	18,55
VIII	2,24	341	0,03	5,19
		336	0,07	6,35

TABLE 2. Calculated Characteristics of Imides with Different Structures*

Struct.	E_π	ΔE_π	E_{VR}	$\frac{E_{VR}}{n}$	ΔE_{int}	$\Delta E_{int}/m$	$\varepsilon_{v.o.}$	$\varepsilon_{l.v.}$	p_{N-Ar}	$\Sigma\delta^+$
I	12,459	0,749	3,775	0,4719	—	—	−11,051	−3,422	—	0,544
Ii	11,710		3,480	0,4350	—	—	−10,673	−3,300	—	—
II	23,172	0,580	7,864	0,5617	0,655	0,655	−9,823	−3,511	0,280	0,582
IIi	22,592		7,738	0,5527	0,824	0,824	−9,483	−3,506	0,378	—
III	20,377	0,790	7,237	0,6031	—	—	−10,734	−2,972	—	0,555
IIIi	19,587		6,901	0,5751	—	—	−10,421	−2,880	—	—
IV	31,096	0,642	11,332	0,6296	0,661	0,661	−9,723	−3,050	0,283	0,592
IVi	30,454		11,144	0,6191	0,809	0,809	−9,345	−3,122	0,368	—
V	52,128	—	19,224	0,6408	1,316	0,658	−9,333	−3,009	0,283	0,593
VI	30,563	—	10,967	0,6093	—	—	−10,998	−3,806	—	0,553
VII	51,988	0,623	19,144	0,6381	1,309	0,655	−9,878	−3,908	0,280	0,590
VIIi	51,365		18,975	0,6325			−9,552	−3,862	0,371	—
VIII	62,770	—	23,242	0,6456	0,661 0,578†	0,661 0,578†	−9,761	−3,458	0,282 0,303†	0,592
IX	93,918	—	34,924	0,6467	1,308	0,654	−9,659	−3,916	0,281	0,591

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*The energy values are given in electron volts.

† These values characterize the carbon–carbon bonds in the diphenyl fragment.

of the molecular diagrams of I with II or III (see Fig. 1). In both cases, one notes an increase in the overall effective positive charge on the atoms forming the C–N bond [$\Sigma\delta^+(\Sigma\delta^+ = \delta_C^+ + \delta_N^+)$], and it is somewhat greater for II.

The electron-acceptor effect of the benzene ring with respect to the imide rings in the case of N-addition of the benzene ring is evident from the overall pattern of the electron-density redistribution. In this case, the mesomeric moment of the N → C_6H_5 group is directed toward the benzene ring and is about 0.5 and 0.6 D for II and IV, respectively (Table 1). The values obtained are somewhat higher than those in the literature [6, 7], but our estimate seems more reasonable to us.

The formation of pyromellitimide structure VI again leads to a certain additional redistribution of the electron density as compared with the additive summation of the charges of the two phthalimide rings. However, the electron distribution characteristics that we obtained do not change further during the formation

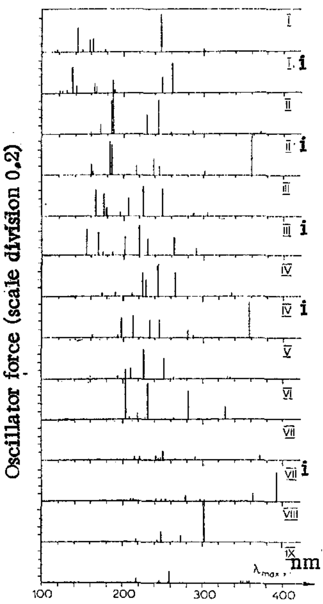


Fig. 3. Calculated energies (λ_{max}) and oscillator forces (f) of the electron transitions to the singlet excited states.

of structures that are most likely realized in polypyromellitimides (see V, VII, and IX) and can be considered to be those for the corresponding fragments of the polymer molecule.

Let us examine the effects of N-phenyl substitution and annelation of the imide ring, as well as an increase in the chain length of the molecule and different methods of bonding the fragments, if this is judged from such computational characteristics as a change in the π-bond energies (E_{π}), a change in the vertical resonance energies (E_{VR}), and a change in some spectral characteristics (Table 2).

Because of the different number of bonds in the molecules being compared, we will compare the effects of N-phenyl substitution and annelation from the resonance energy per π electron, E_{VR}/n. From the data in Table 2 it is seen that, as compared with I, the E_{VR}/n value for III is appreciably larger than for II, which may be evidence for a certain advantageousness in the realization of the phthalimide ring rather than N-phenyl substitution of maleinimide. Transition to IV and then to VII is accompanied by a further increase in E_{VR}/n.

The energy of interaction (ΔE_{int}) of the aromatic rings with the maleinimide, phthalimide, or pyromellitimide rings due to π-electron delocalization is, respectively, 0.655, 0.661, and 0.655 eV and remains practically independent of the chain length of the molecules. A comparison of VII with VIII demonstrates that the N−Ar bond is strengthened somewhat when a pyromellitic acid grouping in the monomer link is replaced by a diphenyltetracarboxylic acid grouping, and the carbon−carbon bond in the diphenyl fragment proves to be considerably weaker than the N−Ar bonds (from the bond orders and ΔE_{int} values).

It is apparent that destructive processes in the polyimides should be accompanied by homolytic and heterolytic cleavage of the bonds. From an analysis of our results with respect to the bond orders, it can be concluded that the $N-C_{Ar}$ bond is weaker than the analogous bond within the ring for homolytic cleavage of aromatic imides, and this relationship is retained for all types of imides and is independent of the length of the macromolecule.

We will use the $\Sigma\delta^{+}$ values as a measure of the tendency of a molecule to undergo hydrolysis, assuming that an increase in $\Sigma\,\delta^{+}$ on the atoms of a bond undergoing hydrolysis favors cleavage of the bond or assists in attack of one of the atoms of the bond by a nucleophilic agent [8]. It then turns out (see Table 2) that structures V, IV, and VII should be hydrolyzed most readily, while I will be the least inclined to undergo hydrolysis.

Electronic Absorption Spectra. Let us compare the calculated energies and oscillator forces of the electron transitions (these data are presented schematically in Fig. 3) with the available experimental data.

It is known [9] that the long-wave absorption band in the UV spectrum of maleinimide has λ_{max} 265 nm ($\varepsilon \simeq 800$, n-hexane) and experiences a long-wave shift on passing to polar solvents. According to the results of calculations (Fig. 1), the long-wave π,π^{*} band is of low intensity and corresponds to a transition to a more polar excited state (Table 1), but is position differs by about 35 nm from the experimentally observed value. It is true that one should make the reservation that the indicated transition possibly should have been compared with the long-wave absorption band of N-alkyl-substituted maleinimide (λ_{max} 300 nm [9]), in which precisely that state of the π-unshared pair of N which was more adequately assumed in the PPP method is realized.

The calculated spectrum of N-phenylmaleinimide contains several long-wave electron transitions that have very small oscillator force values, and all of these transitions are associated with considerable charge transfer from the benzene ring to the imide ring (Table 1). The transition that is of the same nature as the long-wave transition of maleinimide has λ_{max} 242 nm (f 0.797) in N-phenylmaleinimide. The experimental λ_{max} value is 322 nm ($\varepsilon \simeq 400$) [9].

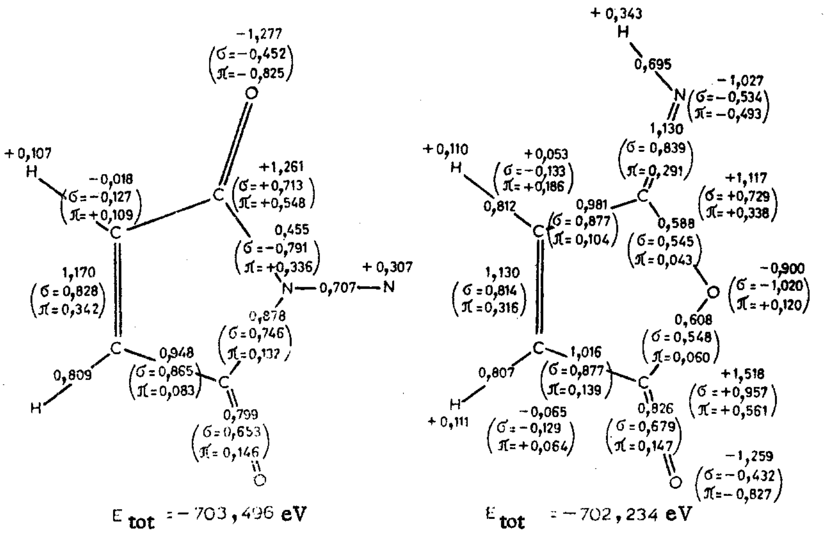


Fig. 4. Molecular diagrams of maleinimide (I) and its isoform (Ii) [extended Hückel method (EHM)].

According to the data in [10], the long-wave absorption band of phthalimide (III) has λ_{max} 297 nm, and Gladchenko and co-workers experimentally ascribed it to a π,π^* transition. Calculation gives $\lambda_{max} \simeq$ 304 nm for the long-wave transition, and this excitation is associated with an increase in the dipole moment to 5.34 D (from 1.95 D in the ground state) (Table 1), and the principal fraction of the charge migrates from the 1 and 4 positions (Fig. 1) of the benzene ring to the carbonyl groups of the imide ring. The charges on the nitrogen atoms do not change. The more intense of the calculated transitions ($\lambda_{max} \simeq$ 248 nm) is accompanied by a still greater migration of the π electrons (μ^{ex} = 8.30 D) to the carbonyl groups, during which the 2 and 3 positions of the benzene rings should be activated.

The structural band of phthalimide fluorescence in alcohol beginning at ~25,000 cm^{-1} (τ ~ 0.55 sec) was observed in [11], and it was noted that its position and the quantum yield are markedly dependent on the nature of the solvent. We obtained a value of ~526 nm for the singlet–triplet splitting, i.e., a value that differs considerably from the experimental value.

We were unable to find data on the absorption or luminescence spectra of N-phenylphthalimide, but calculation demonstrates that the long-wave band in its spectrum should lie 30 nm closer to the visible portion of the spectrum, and, from its nature, it is the band of charge transfer from the benzene ring to the phthalimide ring. The longest-wave transition for which redistribution of charge occurs only in the phthalimide ring has λ_{max} ~ 263 nm and is quite intense.

Pyromellitimide should have long-wave absorption in a region that is still closer to the visible region. This band is shifted bathochromically in N,N'-diphenylpyromellitimide (VII).

Imide–Isoimide Rearrangement. Many authors (see [12, 13], for example) use the concept of imide–isoimide rearrangement in explaining the high yields of CO_2 in the destruction of polyimides, particularly polypyromellitimides, and to explain data on their paramagnetism [14]. Within the framework of the quantum-mechanical examination, there is a possibility for estimating the relative advantageousness of the imide and isoimide forms and the effectiveness of the conjugation of the imide ring in one or the other tautomeric form, for establishing the spectral difference of the forms, the nature of the paramagnetism of polypyromellitimides, etc.

An examination of the molecular diagrams of the isoimide forms (Fig. 2) shows that CO_2 can actually be formed during the destruction of the isoimide ring – the orders of the CO bonds in the CO_2 fragment are a maximum in the ring, while the orders of the bond with carbon are a minimum.

We present a more detailed picture of the distribution of the electron density of the valence layer for the imide and isoimide forms in Fig. 4 for maleinimide (I); the effective charges and bond orders calculated from Mulliken analysis of the extended Hückel method (EHM) MO are presented on the molecular diagrams. An examination of the molecular diagrams demonstrates that the N atom in I has surplus total electron density (δ = 0.455 e), which attests to predominance of its σ-accepting capacity over the π-donor capacity. The electron density was distributed over the orbitals as follows: $2s^{1.400}2p^{2.390}2p^{1.664}$ (compare this with the electronic configuration of the free atom $-2s^22p^12p^2$). Competition between the σ-accepting and π-donor capacities is also observed for the C atoms: predominance of the first effect leads to a charge of $-0.018e$ on C. The carbonyl oxygen atoms are strong acceptors of both σ and π electrons. In this case, a large electron deficit is noted on the C atoms attached to them.

The hydrogen atoms are σ donors with respect to both the sp^2-hybridized C atoms and the nitrogen atoms of the "pyrrole" and "pyridine" types.

The transition of maleinimide to the isoimide form leaves the characteristics of the ring C=C bond practically unchanged. Considerable redistribution of the π component of the electron density occurs: the 3-C and 4-C atoms acquire different polarities, and there is a certain strengthening of the bonds in the 2,3 and 4,5 positions. The newly formed C–O bonds prove to be of lower orders, while the C=N bond should be relatively stronger.

To estimate the relative advantageousness of the imide and isoimide forms of identical compounds we will use the differences in the π-bond energies, $\Delta E_\pi = E_\pi^{\text{imide}} - E_\pi^{\text{isoimide}}$, since the structures being compared are isoelectronic and have the same number of bonds. We will make a comparison of compounds with a different number of electrons with respect to E_{VR}/n. It is seen from the data in Table 2 that the imide forms of all of the investigated imides are more favorable than their iso forms. Individually, N-phenyl substitution leads to a decrease in the advantageousness of the imide forms, while annelation results in a certain increase in ΔE_π, which, however, should not be considered to be a manifestation of the increase in the advantageousness of the imide forms, since an increase in ΔE_π, for example, in III as compared with I, may be a consequence of the presence of a large number of π electrons in III. However, a comparison of III and I, as well as II and I, with respect to E_{VR}/n demonstrates that both N-phenyl substitution and annelation lead to a certain decrease in the advantageousness of the imide forms.

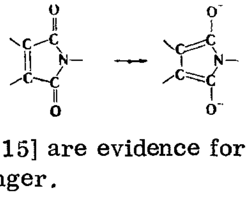
Since simultaneous isomerization of adjacent rings is unlikely in polymeric imides in general and in polypyromellitimides in particular, the effect of isomerization of one of the adjacent imide rings was estimated in the case of VII. Our data show a certain decrease in the advantageousness of the imide structure in this case ($\Delta E_\pi = 0.623$ eV). However, this effect is associated with transition to a new system containing three condensed rings rather than with lengthening of the molecular chain.* One should not therefore expect an increase in the relative advantageousness in polypyromellitimides.

In the case of maleinimide we verified whether the conclusion regarding the advantageousness of the forms when the σ-valence electrons are taken into account is a legitimate one. The appropriate calculations were performed within the framework of the EHM. It was found (Fig. 4) that the imide form ($\Delta E_{tot} \approx 1$ eV) is also the more favorable form with respect to the total electron energies (E_{tot}).

The use of the interaction energy (ΔE_{int}) as a measure of the effectiveness of interaction between the benzene and imide rings in the various tautomeric forms [1] (Table 2) is evidence for a stronger interaction with the isoimide rings.

We also arrive at the conclusion that there is stronger conjugation in compounds with rings in the isoimide form on analyzing the calculated absorption spectra, taking the bathochromic character of the long-wave band as a measure of the conjugation. In fact, it is apparent from the data presented in Fig. 3 and Table 2 that the long-wave bands in the spectra of the iso forms of II, IV, and VII are shifted to the red region and are considerably more intense than the bands of the same nature in the spectra of the imides. A comparison of the molecular diagrams of the ground and excited states of the molecules demonstrated that the long-wave absorption is accompanied by charge transfer from the benzene rings to the imide rings.

The results obtained in the present study may be useful for the identification of isoimide forms of the investigated imides. Data on the spectral difference between the imide and iso forms are contained in Fig. 3. For example, in I the long-wave band of the imide is shifted by ~40 nm to the red region and is of much lower intensity than the corresponding band in Ii. The long-wave absorption in both forms is accompanied by this sort of migration of the electron cloud, which can be depicted as



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*The results of our previous studies [1, 15] are evidence for the invariance of the energy characteristics of the molecules as their chains grow longer.

The following electron transitions in I and Ii are also of the same nature – the π-electron density is concentrated on the C =C bond, and the transitions have approximately the same energy (λ_{max} 247 nm) but differ in intensity by a factor of three. A comparison of the calculated spectra (Fig. 3) demonstrates that the tautomeric forms are spectrally different in the remaining investigated imides. If the iso form were present in appreciable concentrations in real imide systems, it would therefore be detected by UV spectoscopy.

Proceeding from the energy difference between the isoimide and imide forms ($\Delta E \sim 0.6$ eV) calculated in this study, we will estimate their concentration ratio. Thus at room temperature this ratio is $\sim 10^{-10}$. The explanation of the starting paramagnetism of aromatic polypyromellitimides invoking the concept of isomerization of the imide rings should therefore be considered to be absolutely groundless, especially because there is no need for this, since, as demonstrated above, the imide ring itself participates quite effectively in conjugation.

At higher temperatures (400-500°) the concentration of the iso form increases considerably, but it remains inadequate (10^{-5}-10^{-4}) to explain the formation of CO_2 during the destruction of polypyromellitimides by disintegration of the isoimide rings. It therefore seems more valid to us to associate the formation of CO_2 with the incompleteness of cyclization in polyimides [16] and with the possibility of hydrolysis of the imide ring with subsequent decarboxylation.

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