RELATION BETWEEN CONFORMATIONAL STRUCTURE, VIBRATIONAL SPECTRA AND INTRAMOLECULAR EXCIMER FORMATION IN 2,4-DIMETHYL-2,4-DIPHENYLPENTANE

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ABSTRACT

Conformational energy calculations on 2,4-dimethyl-2,4-diphenylpentane have been performed with explicit allowance for methylene bond-angle flexibility. The value of this angle which minimizes the energy is close to 126° , whatever the conformation. The energy contours are given versus main chain bond rotations. An intramolecular mobility study reveals that two kinds of motions are expected: the first includes motions with low activation energies while motions of the second group require a much higher activation energy and involve a large rotation around C—C skeleton bonds. In all cases the phenyl ring rotations are rather strongly coupled with the chain rotations.

IR analysis and intramolecular excimer formation indicate that 2,4-dimethyl-2,4diphenylpentane exists in one of the most stable conformations in the crystalline state. In the liquid state higher-energy conformers are present. Fluorescence emission studies show that 2,4-dimethyl-2,4-diphenylpentane exhibits a higher efficiency of excimer formation than 2,4-diphenylpentane, because of the rather small energy barrier between the excimer and the ground-state conformations.

INTRODUCTION

A knowledge of local conformation and molecular motions provides an interesting approach to study the physical properties of a molecule. Different methods have been proposed for this purpose. Among these, conformationa energy calculations give theoretical information on the preferred conformations and intramolecular mobility. From an experimental point of view, a valuable approach relies on the sensitivity of specific vibrational modes of the molecule to different conformations of the chain and to intramolecular excimer formation which is characteristic of a specific conformational structure.

Previous work [1-3] on 2,4-diphenylpentane, 2,4,6-triphenylheptane and 2,4,6,8-tetraphenylnonane gave experimental evidence of the influence of the local alkyl-chain conformation on some normal modes of the benzene ring and proved that an isotactic conformation of the chain is more favourable

for intramolecular excimer formation than a syndiotactic conformation [4].

The present paper deals with the conformational structural analysis of 2,4-dimethyl-2,4-diphenylpentane (DMDPP) which possesses a bulky methyl group on the α -carbon compared with 2,4-diphenylpentane (DPP).

EXPERIMENTAL

DMDPP was prepared by reaction of neophyle chloride on cumyl potassium.

IR spectra were recorded with a Nicolet FT 7199 Fourier Transform infrared spectrometer. The number of scans was 200 and a resolution of 2 cm⁻¹ was used. Raman spectra were obtained with a Jobin—Yvon Ramanor Laser Raman spectrometer equipped with an He—Ne laser ($\lambda = 5145$ Å).

Absorption spectra were recorded on a Cary Model 15 spectrometer and emission spectra obtained on a Fica Model 55 Mk II spectrofluorimeter equipped with a 450 xenon lamp and an R 212 photomultiplier tube. Emission spectra were automatically corrected for instrumental response; the excitation wavelength was about 260 nm. The optical density of all solutions was 0.1 at 260 nm. Measurements were made on solutions carefully degassed by a repetitive freeze—pump—thaw cycle. A Dupont Curve Resolver (Model 310) was used to analyze the fluorescence spectra.

RESULTS AND DISCUSSION

After consideration of the conformational energy calculations, the experimental results for vibrational analysis and fluorescence excimer formation will be discussed.

Conformational energy of DMDPP

The conformational energy of DPP has been computed earlier [5], with the assumption of rigid bond angles equal to the tetrahedral value for sp^3 carbon atoms. However, in the case of DMDPP, the substituent bulkiness and position are such that this assumption leads to very high energies. Moreover, the conformational energy minima are then separated by potential barriers high enough to prevent any rotation around aliphatic C—C bonds. However, X-ray analysis [6] and conformational energy calculations [7] on molecules which experience steric repulsions similar to those existing in DMDPP have shown that the C—CH₂—C methylene bond angle may be strongly distorted, while other bond angles remain close to 110°.

We have thus taken account of methylene bond-angle flexibility in calculation of the conformational energy of DMDPP. The position and energy of the preferred conformations have been examined and the intramolecular mobility studied.

Method of calculation

Methyl groups have been treated as spherically symmetrical bodies in order to reduce to five the number of independent coordinates that generate a given conformation (Fig. 1): two rotation angles on the chain skeleton $(\phi_1 \text{ and } \phi_2)$, two rotation angles for the phenyl group $(\Psi_1 \text{ and } \Psi_2)$, and the central chain bond angle θ_1 . Angles ϕ_1 and ϕ_2 are taken as 0° in the *trans* conformation, while Ψ_1 and Ψ_2 are equal to 0° when the α -methyl group lies in the ring plane. The positive sign is shown on Fig. 1.

The distortion of angle θ_1 leaves the methylene hydrogen atoms in the bisecting plane of θ_1 symmetrical with respect to the C—C—C chain bond plane. The bond angles relative to carbon atoms 1 and 3 are taken equal to the tetrahedral value and fixed values are assigned to the bond lengths [5].

The calculation of potential energy has been carried out by summing the following terms.

(1) Van der Waals' interactions between atoms separated by more than two bonds. These interactions were calculated using the Buckingham potential function

 $E(R) = A \exp(-BR) - CR^{-D}$

Values assigned to constants A, B, C and D are given in ref. 5.

(2) The torsional energy of rotation around C-C bonds of the main chain, estimated from the formula

$$E=\frac{V_0}{2} (1-\cos 3\phi)$$

where V_0 is equal to 2.7 kcal.



Fig. 1. DMDPP molecule in the all-trans conformation.

(3) The electrostatic energy. Given two point dipoles $\vec{\mu_i}$ and $\vec{\mu_j}$, separated by the vector \vec{a} , the mutual potential energy is given by

$$E = \frac{1}{\epsilon} \left[\frac{\vec{\mu}_i \cdot \vec{\mu}_j}{a^3} - \frac{3(\vec{\mu}_i \cdot \vec{a})(\vec{\mu}_j \cdot \vec{a})}{a^5} \right]$$

The dielectric constant ϵ has been given the vacuum value. The $\overrightarrow{\mu}$ vectors are located at the centre of each phenyl ring, pointing along the bond between chain and ring, and have a value of 0.43 D as measured for cumene. (4) The θ_1 distortion potential function is given by

$$E = k(\theta_1 - \theta_{10})^2/2$$

where θ_{10} is the zero-strain value of θ_1 , and was taken to be 109°28'. The k elastic constant has been given the value 136 kcal rad⁻², close to the values found from IR data [8].

The tt conformation of meso-DPP

The calculations already performed [5] have shown that in the preferred conformations of both DPP isomers the phenyl rings are far from each other except in the almost tt conformation of the *meso* isomer, where the two phenyl rings are opposite but close to each other. In this case, where the strain of the angle θ_1 is the strongest, we have investigated the conformational energy surface when allowance is made for the flexibility of θ_1 . The results indicate that the location of the energy minimum is insensitive to θ_1 when it is varied between 110° and 120°. On the other hand, the absolute minimum of energy is obtained for $a \theta_1$ value of about 112–114° (Fig. 2), that is the same value as Suter and Flory [9] obtained for polypropylene, and Panov et al. [10] for isotactic polystyrene. This increase of angle θ_1 leads to only a small decrease of conformational energy, less than 1 kcal.



Fig. 2. Conformational energy of the preferred conformations of *meso*-DPP and DMDPP versus the methylene bond angle.

Thus even with such a compact conformation, the assumption of rigid and tetrahedral bond angle is adequate. The same analysis applied to conformation $g^{-}t$ leads to the same result for θ_1 , with a decrease of energy still lower (Fig. 2).

Preferred conformations and intramolecular mobility of DMDPP

This molecule has no asymmetric carbon atom and thus does not show optical isomerism. Four different minima are identified, noted I, II, III, and IV on the contour map shown in Fig. 3. The angle θ_1 was varied by increments of 2° in the vicinity of these preferred conformations and the curves of Fig. 2 were obtained. The shape of the plot of minimum energy versus θ_1 is very similar for all four conformations; the energy increases by about 1.5 kcal for a 4° distortion from the best θ_1 value. For conformations I, II, and III, this energy is minimized for a θ_1 value of about 126°. Conformation IV alone exhibits a minimum for a slightly higher value, close to 128°. A schematic representation of these conformations is given in Fig. 4.



Fig. 3. Potential energy contours of DMDPP as a function of main chain bond rotations. The sign + denotes a local minimum and \succeq denotes a saddle point.



Fig. 4. Conformations of DMDPP.

However, taking into account the assumptions already made, it was assumed that θ_1 is constant at 126° whatever the angles ϕ and Ψ . Then, the conformational energy of the molecule was computed by varying ϕ and Ψ in 10° increments. Energy contours given in Fig. 3 versus ϕ_1 and ϕ_2 have been obtained by associating each pair (ϕ_1 , ϕ_2) with the pair (Ψ_1 , Ψ_2) which minimizes the energy. This map exhibits two symmetry axes and one symmetry centre, so the energy can be obtained for any values of ϕ_1 and ϕ_2 (Fig. 5). The location and energy of preferred conformations are given in Table 1. Although the absolute values of these energies are, of course, higher than those found for DPP, the differences between them are similar for both DPP and DMDPP. It may be seen that, as for DPP, the all-*trans* conformation I has the lowest energy of all. However, unlike DPP, the angles Ψ_1 and Ψ_2 may be far from 0°, as expected from the introduction of two identical CH₃ groups bonded to carbon atoms 1 and 3.

The study of intramolecular mobility was carried out as follows. In order to follow the path of least energy between two preferred conformations, a distortion of angle ϕ_1 or ϕ_2 was made and then the energy was minimized with respect to (ϕ_2, Ψ_1, Ψ_2) or (ϕ_1, Ψ_1, Ψ_2) . This means that the molecule follows valleys of the contour surface, going through saddle points which are



Fig. 5. Location of the conformational energy minima in the plane (ϕ_1, ϕ_2) of the main chain bond rotations; the symmetry axes are denoted by dashed lines and the symmetry centres by \bullet .

TABLE 1

Values of the internal rotation an	ngles and energy of the	preferred conformations of DMDPF
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	ϕ_1	φ ₂	Ψ_1	Ψ_2	E (kcal)	
ī	0		0	20	24.7	
п	-130	-20	70	20	26.0	
ш	10	-110	-10	40	25.7	
IV	-140	100	80	40	27.4	

located on Fig. 3. Taking into account the symmetry elements, several angles can lead to any conformation (I, II, III or IV) as shown in Fig. 5. From angles corresponding to conformation II, for example, one can reach another conformation, say I, using several angles which lead to I. As a consequence, one can follow different routes corresponding to different energy barriers. The lowest energy barrier is related to the lowest angle change from the initial state. The final state will be denoted, arbitrarily, by a prime.

In Table 2 are listed the activation energies needed to go from one of the states I, II, III, IV to a neighbouring state. For states I, II, and IV, the transition may occur between two symmetrical conformations so that the energy difference between them is zero. If 7 kcal is taken to be the maximum barrier height a molecule can undergo at room temperature, it may be seen that several rotations are allowed, such as the transitions $I \rightarrow I'$, $IV \rightarrow IV'$ and $I \rightarrow III'$.

Figure 6 depicts how angles Ψ_1 and Ψ_2 vary when the molecule undergoes conformational motion. It indicates that phenyl ring rotation and chain rotation are interdependent: when angle ϕ is distorted, the phenyl rings must rotate even if the initial and final values of Ψ are the same, as for example Ψ_2 in the course of transition I \rightarrow II.

TABLE 2

Activation energies between the stable conformations of DMPP

	I	II	ш	IV
<u> </u>	1.5	7.5	5.5	
II'	8.8	7.9	9.2	7.8
111′	6.3	8.9	_	_
IV'		10.5	—	2.1



Fig. 6. Phenyl ring rotations in the course of transition between the preferred conformations.

Large-amplitude rotation of Ψ may occur when the phenyl rings and the methyl groups are coplanar. Note that this conformation is then the maximum energy conformation and is assimilated in a saddle point. Several examples are provided by transitions II \rightarrow III for Ψ_1 or II \rightarrow IV for Ψ_2 .

Vibrational analysis

Vibrational spectroscopy proved to be a valuable tool to detect conformational changes in molecules and has been widely used for this purpose. As far as DPP and its homologues are concerned, the 16b out-of-plane normal mode of the benzene ring appears as a strong IR absorption band at 540 cm⁻¹ when the benzene ring (the notations used are according to Varsanyi [11]) has an environment of at least four aliphatic carbon—carbon bonds in the *trans* conformation. When the number of successive alkyl links in the *trans* conformation is less than four, the absorption band is observed around 555 cm⁻¹. In contrast, the 10b out-of-plane normal mode, which appears in the range 150— 200 cm⁻¹, is sensitive to the length of the alkyl-chain conformation and a detailed discussion of this effect is given elsewhere [2, 3].

A Raman study of the same compounds [12] indicated the sensitivity of vibrations 1 and 13 of the benzene ring to the local conformation of the chain. We will now consider the behaviour of these four modes in DMDPP.

16b out-of-plane vibration

This vibration appears as an absorption band located around 540 cm⁻¹ in many monosubstituted alkylbenzenes. Experimental spectra for tertbutylbenzene in the range 500—600 cm⁻¹ at room temperature and for DMDPP in the crystalline and liquid states at different temperatures are given in Fig. 7. Tert-butylbenzene, which does not exhibit conformational isomerism, presents only one absorption band at 548 cm⁻¹ corresponding to the 16b mode. On the other hand, two absorption bands are observed in the same region of the spectrum for crystalline DMDPP, at 534 cm⁻¹ and 557 cm⁻¹.

Previously calculated conformational energies (Table 1) suggest that the most stable structures, I or III, could exist in the crystalline state. However, as will be discussed later, the absence of intramolecular excimer formation in the crystalline state indicates that form III exists in this state. The presence of only one conformational structure implies only one absorption band for the 16b mode. Besides the 16b mode, the 6a radial skeletal vibration of the ring could give rise to an absorption band above 500 cm^{-1} as it varies greatly in monosubstituted benzenes ($300-530 \text{ cm}^{-1}$) [11]. As will be shown later, the Raman spectrum permits assignment of the 557-cm^{-1} absorption band to the 16b mode while the 534-cm^{-1} absorption band is relevant to the 6a vibration. On melting, destruction of the crystalline structure results in the appearance of conformational structures of higher energy (forms II and IV in Table 1 and Fig. 4). This in turn should result in an increase in frequency of the 16b mode for these conformers if similar behaviour to that observed for DPP [1] holds for DMDPP. Experimentally, three absorption bands are



Fig. 7. IR spectra of tert-butylbenzene (1) and DMDPP (2) in the range $500-600 \text{ cm}^{-1}$ as a function of temperature: (2a) crystalline; (2b) 25° C; (2c) 50° C; (2d) 75° C; (2e) 100° C; (2f) 135° C; (2g) 160° C.

Fig. 8. IR spectra of liquid DMDPP in the range 500–600 cm⁻¹: (1) 25°C; (2) 160°C; (3) digital subtraction (2) – (1). Subtraction based on the elimination of the conformationally insensitive absorption bands in the region 800–1000 cm⁻¹.

observed between 500 and 600 cm⁻¹, at 537, 561 and 567 cm⁻¹. The 537cm⁻¹ and 561-cm⁻¹ absorption bands are assigned to the 6a and 16b normal modes of form III in the liquid state, respectively. The 567-cm⁻¹ band is assigned to the 16b mode of the benzene rings involved in conformational structures II and IV. This assignment is confirmed by the evolution of the spectra with respect to temperature: as expected, an increase in temperature (Fig. 7) induces an increase in the amount of the less-stable conformation, which is experimentally observable as an increase in the relative intensity of the 567-cm⁻¹ absorption band. Note that the vibrational spectrum is no help in distinguishing forms II and IV.

A digital subtraction of the spectra obtained at 25° C and 160° C (Fig. 8) indicates a decrease in intensity of both the $537 \cdot \text{cm}^{-1}$ and the $561 \cdot \text{cm}^{-1}$ absorption bands as the temperature increases. This result shows that the 6a mode is also conformationally sensitive. However, although this mode is observable for the III form at 537 cm^{-1} , it was impossible to identify the corresponding absorption bands for conformational structures II and IV, which must overlap other absorption bands.

To support the previous assignments, consider the Raman spectrum of DMDPP (Fig. 9) in the range 500—600 cm⁻¹. A weak Raman line is observed at 559 cm⁻¹ and 567 cm⁻¹ (depolarized) in crystalline and liquid DMDPP, respectively. These lines are easily assigned to the 16b (B_1) normal mode of the ring. Two other Raman lines of medium intensity are observed in the same range in DMDPP at 530 and 521 cm⁻¹. On melting a completely polarized broad line appears at 526 cm⁻¹. This line has obviously to be assigned to the 6a (A_1) normal mode of the ring as well as the 530-cm⁻¹ line in the crystalline state. The crystalline 521-cm⁻¹ line remains unassigned but could result from a combination of lower-frequency vibrational modes in the crystalline state.

10b out-of-plane vibration

The 10b mode occurs in the range $150-200 \text{ cm}^{-1}$ in monosubstituted alkylbenzenes [11]. It appears as a strong-to-medium line in the Raman effect which is a particularly convenient method for the study of this spectral range. This mode was observed as conformationally sensitive in DDP [2]. Raman spectra of crystalline and liquid DMDPP are shown in Fig. 9. In the crystalline compound, two Raman lines are observed at 192 cm⁻¹ and 209 cm⁻¹; these two lines could be tentatively assigned to the 10b vibration



Fig. 9. Raman spectra of DMDPP: (1) crystalline; (2) liquid at 25°C.

Fig. 10. UV absorption spectra of (----) DMDPP and (---) tert-butylbenzene in iso-octane at room temperature.

 (192 cm^{-1}) and the methyl torsion (209 cm^{-1}) in the same way as for DPP [2].

On melting, it was expected that an additional Raman line would appear in the lower-frequency range [2], but no such spectral feature appeared and only one broad line was observed around 200 cm⁻¹. This result does not imply insensitivity of the 10b mode to the conformation, as the Rayleigh line can overlap the Raman line which corresponds to structures II and IV.

Symmetrical ring stretching mode 1 and C-X stretching vibration 13

These two modes were observed as conformationally sensitive in the Raman spectrum of DDP [12]. As far as DMDPP is concerned, no experimental evidence for such an effect was detectable. The v_1 mode appears at 709 cm⁻¹ and the v_{13} mode is observed at 1190 cm⁻¹ in the crystalline and liquid states.

Intramolecular excimer formation

Intramolecular excimer formation studies provide a means of investigating conformational structures in fluid solution. An excimer is an electronically excited complex formed between two identical aromatic groups in an approximately coplanar sandwich arrangement. Hirayama's "n = 3 rule" [13] states that intramolecular excimer formation only occurs when the aromatic chromophores are separated by a chain containing three carbon atoms.

A dilute solution of DMDPP exhibits, in addition to the normal molecular fluorescence appearing at 285 nm and characteristic of the monomer phenyl group, a broad emission band peaking at about 330 nm and assigned to the intramolecular excimer.

Figure 10 shows the absorption spectra at room temperature of iso-octane solutions of DMDPP and of tert-butylbenzene, its model compound. The similarity of the shapes and spectral distribution between the two spectra suggests that little interaction occurs between the two phenyl moieties in the ground state of DMDPP.

The fluorescence spectra of DMDPP and tert-butylbenzene are compared in Fig. 11a. Figure 11b shows the emission spectra of *meso-* and *dl-DPP*, the respective model compounds of isotactic and syndiotactic polystyrenes for which we have previously discussed intramolecular excimer formation [4, 14]. All emission spectra were recorded under identical conditions, on degassed iso-octane solutions, concentration-matched for equal light absorption. Excimer fluorescence of DMDPP is very similar in spectral structure (band position and band shape) to that of 2,4-diphenylpentanes.

Excimer formation involves rotational motion about the carbon—carbon bonds of the methylene linkage to achieve a conformation in which the two aromatic groups overlap in a nearly face-to-face arrangement. Thus, excimer formation is related to the height of the energy barrier between the groundand excimer-state conformations. Measurements of the ratio of the excimerto-monomer emission intensities, I_D/I_M , as a function of temperature yield



Fig. 11. Corrected fluorescence spectra of degassed iso-octane solutions at 25° C. a – (1) DMDPP; (2) tert-butylbenzene. b – 2,4-Diphenylpentanes; (3) meso isomer; (4) dl isomer.

the activation energy required to surmount the rotational barrier. The slope of the linear part of the curve shown in Fig. 12 gives an apparent activation energy of 4.1 kcal mol⁻¹ for intramolecular excimer formation in the lowtemperature range (+ 30 to -20° C). The temperature dependence of excimer and monomer bands is shown in Fig. 13. Below 30°C, the intensity of the excimer band decreases a little while the intensity of the monomer band increases greatly. Above 30°C, both emission bands slightly decrease, the decrease of the excimer fluorescence intensity exceeding somewhat that of



Fig. 12. Temperature dependence of the ratio of excimer-to-monomer fluorescence intensities of DMDPP in iso-octane.



Fig. 13. Temperature dependence of fluorescence intensity of excimer (I_D) and monomer (I_M) bands for DMDPP in iso-octane (in arbitrary units).

the monomer emission band. Excimer dissociation is responsible for the decrease of the excimer emission band above 30° C but, as in the case of diphenylpentanes [14], there is no corresponding increase in intensity of the monomer fluorescence band, which indicates that excimer dissociation does not lead to an excited monomer. However, the excimer in DPP has a higher stability than in DMDPP since the excimer intensity decreases above 50° C for the *dl* and above 60° C for the *meso* isomer.

The ratio I_D/I_M is an interesting parameter. This ratio, calculated from band areas, is an approximate measure of the overall efficiency of excimer sampling; its value is 3.83, 2.22 and 0.37 for DMDPP, *meso* and racemic DPP, respectively, in iso-octane solutions at 25°C.

These data clearly show that excimer formation is more efficient for DMDPP than DPP. This result is surprising in view of the additional interaction between the two α -methyl groups in the former compound. As seen above, the conformational energy calculations show that in DMDPP the value of the methylene bond angle which minimizes the energy is close to 126°, a value significantly larger than the 112–114° found for DPP. The distortion of the methylene bond angle leads to deviation from the parallel sandwich arrangement and to a distance between the two aromatic nuclei which is larger than in DPP. Thus a maximum π -orbital overlap is probably not allowed in DMDPP, which could explain the difference in excimer stability between DPP and DMDPP. If the variation of the methylene bond angle explains the lesser stability of excimer conformation in DMDPP, it does not explain the high efficiency of excimer formation in this compound. The fluorescence spectra of crystalline DMDPP exhibits only normal fluorescence; this indicates that structure I, which is the excimer-forming site, is not present in the solid state.

IR studies indicate that III is probably the only form which exists in crystalline DMDPP. From Table 2 it is clear that excimer state I' may only be attained by rotation of conformations II or III, corresponding to the transitions II \rightarrow I' or III \rightarrow I'. The value of the experimental activation energy found agrees well with the latter transition.

As compared with DPP, form III corresponds to the tt conformational state of the racemic isomer, and I to the excimer conformation of DPP.

Conformational analysis by Gorin and Monnerie [5] for racemic DPP has shown that the rotational process is difficult between the tt and excimer g^{t} (or tg^{+}) conformations, and fluorescence emission studies experimentally support this conclusion [4, 14]. The fact that DMDPP exhibits a rather large efficiency of excimer formation with regard to DPP is probably due to the small energy barrier between conformations III and I'.

SUMMARY AND CONCLUSIONS

Conformational energy calculations on DMDPP with explicit allowance for methylene bond-angle flexibility give a best value of 126° for this angle, significantly larger than the angle of $112-114^{\circ}$ that has been found for DPP. The energy differences between the preferred conformations are similar to those found in DPP.

IR analysis of the conformationally sensitive 16b out-of-plane normal mode of the benzene ring which appears in the range 530-560 cm⁻¹, as well as intramolecular excimer formation, indicate that this compound exists in one of the most stable conformations in the crystalline state. In the liquid state higher-energy conformers are present.

Fluorescence emission studies reveal a difference in excimer stability between DMDPP and DPP which may be explained by distortion of the methylene bond angle in the former compound. In contrast, DMDPP exhibits a higher efficiency of excimer formation than DPP because of the rather small energy barrier between the excimer and ground-state conformations.

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