# Spectroscopic studies of compounds containing a P—H bond
## 4.* Vibrational spectra and conformational multiformity of di-*tert*-butylphosphorous acid molecules

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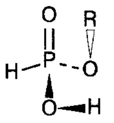
IR and Raman spectra of liquid di-*tert*-butylphosphorous acid and its two low-temperature crystalline modifications are studied. It is found that at least three stable conformations of acid molecules can exist in the liquid state.

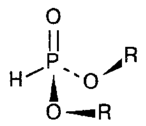
**Key words:** di-*tert*-butylphosphorous acid, conformations, vibrational spectra.

The possible self-association of hydrophosphoryl compounds *via* a hydrogen bond mechanism has previously been reported[1—7] and caused considerable interest in studying the nature of the substantial broadening of the absorption bands of ν(PH) stretching vibrations in IR spectra (see Refs. 1—7). Our studies[5—7] led us to the conclusion that the conformational non-uniformity of the corresponding molecules plays a substantial role. Studying the vibrational spectra of dialkylphosphorous acids (DAPA) $(RO)_2P(O)H$ (R = Me, Et, $Pr^n$, $Pr^i$, $Bu^n$, or $Bu^i$), we have found[6,7] that internal rotation around the P—O bonds occurs in these molecules. In terms of the common conception of crossed-eclipsed forms, six groups of conformers, which differ in the orientation of the OR groups relative to the P=O bond (*gauche,gauche* (GG), *gauche,gauche'* (G'G), *gauche,gauche'* (GG'), *trans,gauche* (TG), *trans,gauche'* (TG'), and *trans,trans* (TT)), should be expected for DAPA molecules.

In the works published previously,[6,7] only three conformations (GG, G'G, and TG) were found. Each of these forms is characterized by its ν(PH) band: ~2470 cm$^{-1}$ (G'G), ~2440 cm$^{-1}$ (GG), and below 2430 cm$^{-1}$ (TG).[7] In the spectra of the liquids at room temperature, the peaks of different conformers coalesce into one broad unresolved peak, as a rule, with a maximum at ~2430—2440 cm$^{-1}$.

In the spectroscopic analysis of the intermolecular interactions of DAPA, in order to rule out the effect of internal rotation on the ν(PH) bands and thus to observe "pure" association effects, it is desirable to study conformationally uniform compounds.


GG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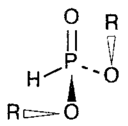
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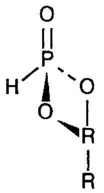
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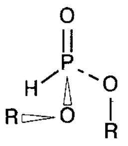
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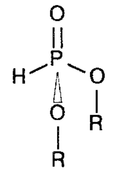
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Di-*tert*-butylphosphorous acid (DTBPA) molecules differ from those of previously studied DAPA[5—7] by their large steric capacity and, according to the available literature data,[8] they exist only in the GG conformation. Therefore, an "unusual" single (*i.e.*, fairly narrow) ν(PH) band should also be expected.

The frequency of the maximum of the ν(PH) band in the experimental spectra of liquid DTBPA at room temperature (Figs. 1 and 2) is lower (~2420 cm$^{-1}$) than those of other acyclic DAPA (~2430—2440 cm$^{-1}$), and its half-width, in fact, is only ~45 cm$^{-1}$ instead of the usual ~70 cm$^{-1}$. It is evident that the bulky *tert*-butyl

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[*] For report 3, see *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 564 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 489 (Engl. Transl.)].

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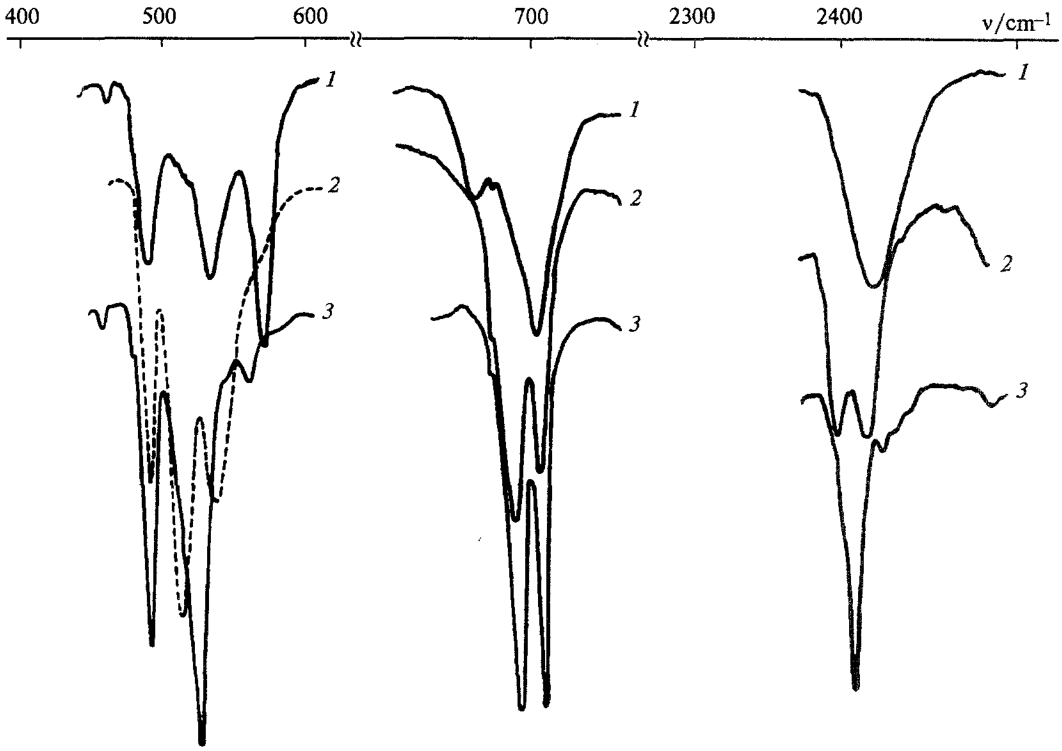

**Fig. 1.** Conformationally sensitive ranges in the IR spectrum of DTBPA: *1*, liquid; *2*, crystal 1; *3*, crystal 2.

groups reduce the fraction of conformers that cause the appearance of high-frequency components of the complex ν(PH) band. However, the agreement between the experimental and expected data stopped at this point. Unexpectedly, pronounced evidence for substantial conformational multiformity was observed in the spectra.

The DTBPA molecule possesses 87 vibrational degrees of freedom ($3N - 6$, where $N$ is the number of atoms). Omitting the frequencies of the methyl group vibrations [stretching ν(CH) (3100—2800 cm$^{-1}$, 18 vibrations), bending δ($CH_3$) (1500—1300 cm$^{-1}$, 18 vibrations), rocking ρ($CH_3$) (900—800 cm$^{-1}$, 12 vibrations),

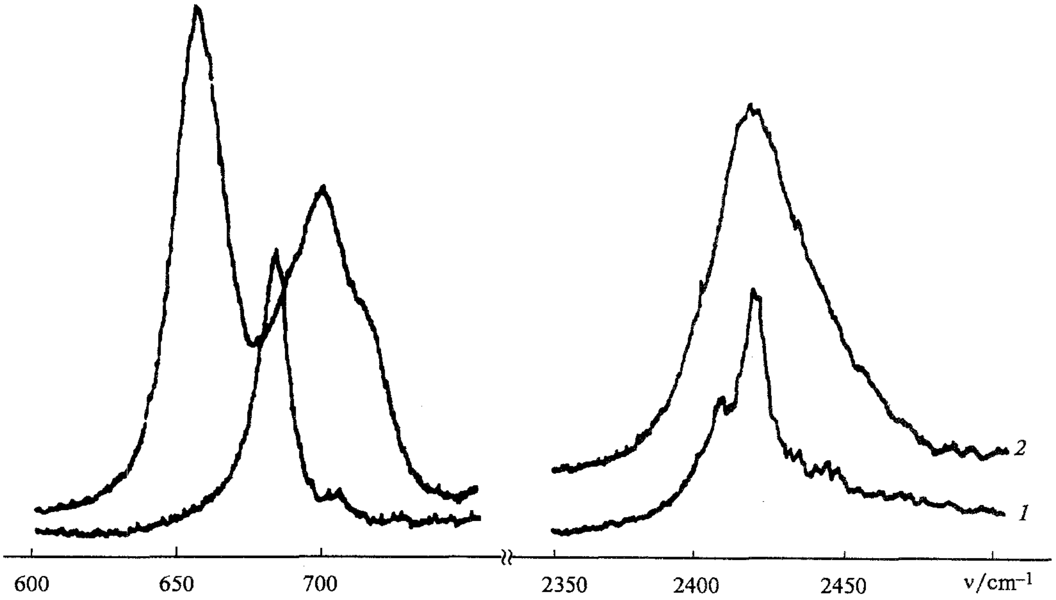

**Fig. 2.** Some conformationally sensitive ranges in the Raman spectra of DTBPA: *1*, crystal; *2*, liquid.

and torsional $\tau(CH_3)$ (200—100 cm$^{-1}$, 6 vibrations)], not more than 33 peaks corresponding to the skeletal vibrations of the molecules should be observed in the spectra. In fact, at least 43 peaks are observed in the Raman spectra of liquid DTBPA outside the mentioned frequency ranges of $CH_3$ groups. The "excess" bands can hardly be assigned to overtones and composite frequencies, because the latter are usually not very active in Raman spectra.

The $\nu$(PH) peak in the spectrum of the liquid has a complicated structure. A comparison of its shape in the Raman spectra under different polarizations of the exciting irradiation reveals four components: 2465, 2445, 2421, and 2413 cm$^{-1}$. The $\nu$(PH) IR band is also asymmetric, exhibiting a shoulder at ~2430—2440 cm$^{-1}$.

When liquid samples are colled to −10 to −20 °C, the spectra change sharply (bands broaden, intensities redistribute, vibrations of the crystalline lattice appear in the Raman spectra, *etc.*), attesting to DTBPA crystallization. In this case, many Raman lines (239, 311, 656, 695, 700, 980, 1069, and 1190 cm$^{-1}$) and several IR bands (563, 657, and 1065 cm$^{-1}$) are "frozen out", the high-frequency wing of $\nu$(PH) (~2430—2440 cm$^{-1}$) disappears, and two narrow peaks appear instead of the broadened asymmetric band: 2400 and 2418 cm$^{-1}$ (IR); and 2408 and 2418 cm$^{-1}$ (Raman) (see Figs. 1 and 2). This crystalline modification is denoted as "crystal 1" in further discussions.

Another crystalline modification of the substance (denoted as "crystal 2") was obtained by slower cooling of a DTBPA liquid film placed between KBr plates. The IR spectrum of crystal 2 differs noticeably from that of crystal 1. In particular, only one peak at 2410 cm$^{-1}$ remains in the spectrum of crystal 2 instead of the two peaks of $\nu$(PH) of crystal 1. In addition, the bands at 510 and 530 cm$^{-1}$ disappear and a band at 520 cm$^{-1}$ appears instead (see Fig. 1).

The described changes in the spectra are typical of molecular conformational non-uniformity, although it cannot be excluded that intermolecular interactions play a certain role. The crystallization of the substance results in freezing out of at least one of the conformers that exist in the liquid, which causes the disappearance of the corresponding bands from the spectra. Judging from assignments made for other DAPA[7] and the acids mentioned above, the GG and G′G type conformers should cause the high-frequency components of the complex $\nu$(PH) band. However, the existence of DTBPA molecules in the G′G conformation seems to be impossible due to its extreme steric overload capacity. Therefore, the absence of the $\nu$(PH) shoulder at ~2430—2440 cm$^{-1}$ in the spectra of the crystals most likely attests to freezing out of the GG type conformers.

It should be mentioned that no pronounced dynamics of a redistribution in the intensity of the spectral peaks is observed when the liquid is cooled. This means that the energies of the different conformers in liquid DTBPA are close to each other.

We also studied the effect of the polarity of the medium on the IR and Raman spectra of DTBPA. It turns out that the intensity of the IR bands at 563 and 657 cm$^{-1}$, which are frozen out in the crystalline state, decreases compared that of the band at 700 cm$^{-1}$ on going from a DTBPA solution in $CCl_4$ ($\varepsilon$ = 2.21) to one in acetone ($\varepsilon$ = 20.40). Apparently, increasing the medium polarity results in the stabilization of the polar forms of the DTBPA molecules and a decrease in the fraction of conformers with low dipole moments (DM). According to the data obtained previously,[8] it is the GG form of the possible conformers of DTBPA that has the lowest DM. Therefore, the decrease in the intensity of the bands at 563 and 657 cm$^{-1}$ in the spectra of the acetone solutions of DTBPA agrees well with their assignment to weakly polar conformations of the GG type. It should be mentioned that it appears that DTBPA does not become conformationally uniform even after the GG conformer in crystal 1 is frozen out. This is indicated by the fact that the spectrum of crystal 2 has fewer bands than that of crystal 1 due to the additional freezing out of the bands at ~2400 and ~500 cm$^{-1}$ (see Fig. 1). It is likely that these bands belong to conformers that exist in crystal 1 but are frozen out in crystal 2. In this case, crystal 1 must consist of at least two different conformers, and DTBPA molecules can exist in the liquid phase in at least three stable conformations.

Additional analysis, in particular, theoretical estimations of the conformational energy and spectra of the substance, are necessary for the final solution of the problem concerning the number and the structure of DTBPA conformers.

The reasons for the strong disagreement between our data on the conformational uniformity of DTBPA and the conclusions of other authors[8] are worthy of discussion. The latter are mainly based on a comparison of DM values calculated *via* an additive scheme for several possible conformers with experimental DM. It is assumed in the calculations that DM of the $HP(O)O_2$ moiety, which is common for all molecules of the $(RO)_2P(O)H$ series, is independent of the type of R radicals. Meanwhile, the force field of the DAPA molecule changes noticeably not only when alkyl radicals change, but also when there are conformational transformations of the same molecule,[6,7] which attests to the sensitivity of the electronic structure of the DAPA molecule to minor changes in the spatial structure. Like force constants, DM are functions of the electronic structures of molecules. Therefore, the complete additivity approximation previously accepted[8] seems to be inappropriate in this case.

## Experimental

IR spectra were obtained on a Specord 75-IR spectrometer (400—4000 cm$^{-1}$). Raman spectra were recorded on a RTI-30 spectrometer with an Ar$^+$ laser ($\lambda$ = 4880 Å, the spectral width of the gap was 5 cm$^{-1}$, the laser power was 100 mW).

Purity of the substances was checked by IR and $^1$H NMR spectra. Crystalline samples were prepared in cryostats in the instruments, by cooling a film of the substance placed between KBr plates (for recording IR spectra) or a capillary with liquid DTBPA (for recording Raman spectra) with liquid nitrogen. The errors of the determination of the wave numbers corresponding to IR absorption peaks and Raman lines did not exceed ±4 $cm^{-1}$ and ±2 $cm^{-1}$, respectively. DTBPA was prepared by the known procedure.[9] Prior to use DTBPA was distilled at $3 \cdot 10^{-2}$ Torr.

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