PI_3

PI_3^+

PI_3^-

1955

PJ_3 и
AMH_3

R. S. Mulliken.
JACS 77 887
Углы связи в молекулах
типа PJ_3 и MH_3 и их
производных.

PJ_3 < 100°

1688-II

1955

PJ_3. $\Delta_B J_3$ (ν_1. силовые постоянные)

Stammreich H., Forkeris K., Tavares Y.

J. Chem. Phys., 1956, 25, N 5, 580 (англ.)

Спектры комбинационного рассеяния и силовые постоянные PJ_3 и $\Delta_B J_3$.

РЖ., 1957, N 13, 43753

10

2965-III

1963

PCl_3, PF_3, PBr_3, PJ_3, $AsCl_3$, $SbCl_3$ (силовые пост.)

Meisingseth E.

Acta chem. scand., 1963, 17, N 2, 509-512 (англ.)

Calculation of Urey-Bradley ...

РХ., 1964, 8Б33

Ю

1963

PJ_3
I. g

Venkateswarlu K.,
Rajalakshmi K. V.

Indian J. Pure and Appl. Phys., 1963, 1, № 11, 380.

Силовое поле Юри-Бредли и термодинамические св-ва. Пирамидальные молекулы типа XY_3.

см. I.

3703

1964

NF_3; PF_3; PBr_3; PJ_3; $AsBr_3$; AsJ_3

(t.d.f.,)

Nagarajan G.
Indian J. Pure Appl. Phys.,
1964, 2(8), 237-41

Mean applidutes ...

J

4263

1965

PJ_3 ; PJ_4 (структура)

Cowley A. H., Cohen S. T.

Inorgan. Chem., 1965, 4, N8, 1200-204

The iodides of phosphorus. . -

DX 1966 85114

20

$P-J_3$ Chantry G. W. 1966

et al.

J. Chem. Soc. A, n 7, 896.

D_0 Комплексы галогенидов фосфора с галогенидами бора

ч. I ИК-спектры PJ_3

~~соед~~ III $PJ_3 \cdot BJ_3$

J_2PPJ_2, PJ_3 (V.) > P_2J_4 (J. 1967

Frankiss S. G. Miller F. A.; XIII 17-55

Stanford Research Inst., Menlo Park, Calif.

Spectrochim. Acta, Part A, 1967, 23(3), 543-5

Infrared and Raman spectra and structure of P_2I_4

CA, 1967, 66, 20, 89944u

10

1967

РУ$_3$

Коерр G. W., et al.

J. Amer. Chem. Soc., 89, № 14, 3396.

Барьеры инверсии пирамидальных молекул типа XY_3, и родственных плоских молекул, содерж. группу XY.

(см. CH_3^-)

PX_2Y XIII 203 1468

X=F, Cl, Br, J, Y=Cl, Br, J, F (ν_i, среднеквадр. амплит. колеб.)

$AsCl_2Br$, $AsBr_2Cl$

Elvebredd J., Vizi B., Cyvin S., 20

Mueller A., Krebs B.

J. Mol. Struct., 1968, 2(2), 158-60

Mean amplitudes of vibration for mixed halides of phosphorus and arsenic

CA, 1968, 69, n16, 63188n

1968

Müller A., Nieke E.,
Krebs B., Glemser O.

A-1274

есть ф-к

XIII-536 1968

PY_3

Rao P.K., Rao P. B.

Spectrosc. Mol., 17 (190), 8-9

An empirical relation between the mass of the N atom and the rotational distortion constant for XY_3 molecules of symmetry C_{3V} (cm. PH_3) III

1969

PI_3 | Cyvin S.J. и др.

J. Molec. Struct.,

ср-кв. 1969, 4, № 5-6, 341

амплит.

колеб.

(См. NF_3) III

XIII-220 1969

PJ_3^+

PJ_3^-

PJ_3; PJ_2^+

потенциал появления

J^+

до

+1 нб

Ж · 1969 · 21

21 Б100. Связь фосфор — фосфор. Некоторые исследования с помощью электронного удара. Finch Arthur, Hameed A., Gardner P. J., Paul I N. The phosphorus — phosphorus bond: some electron impact studies. «Chem. Communs», 1969, № 8, 391 (англ.)

На масс-спектрометре AEI MS-2H с системой прямого ввода тв. образцов, методом Лоссинга, измерен потенциал появления I^+ из PJ_3^+ (12,7±0,15 *эв*). Вычислены потенциал ионизации PJ_3 (10,45 *эв*) и энергия диссоциации связей PJ_2—J (52 *ккал/моль*) и PJ_2—PJ_2 (73 *ккал/моль*). Прямое определение перечисленных величин затруднено из-за низкого давления паров и термич. нестабильности при повышенной температуре. М. Туркина

(+1) (I)

(+1) (III)

X

Сим. мол $H_3(N, P, As, Sb)$; NHF_2 XIII 330
$D_3(N, P, As, Sb)$; NDF_2 1969
$F_3(N, P, As, Sb)$; $Br_3(N, P, As, Sb)$
$Cl_3(N, P, As, Sb)$; $J_3(N, P, As, Sb)$

King Shin-Tung, Overend J.

J. phys. Chem., 1969, 73, N2, 406-12

10

10

1970

м. п., сил. п. (PF_3, PCl_3, PBr_3, PJ_3, AsF_3, $AsCl_3$, $AsBr_3$, AsJ_3)

KIII 563

Rai S. N., Thakur S. N.,

Austral. J. Chem., 1970, 23, № 5, 881–886 (англ.)

Kinematical evaluation of force constants: application to trihalides of phosphorus and arsenic.

РЖХ 1970 …

PY3 Rai S. N. 1971

Thakur S. N.

сел. Indian. J. Pure and
пост. Appl. Phys. 1971, 9, N1
61-62

(Сел. PA3) III

PBr_3, PI_3,
AsF_3, $AsCl_3$, $AsBr_3$, AsI_3,
SbF_3, $SbCl_3$, $SbBr_3$, SbI_3,
BiF_3, $BiCl_3$, $BiBr_3$, BiI_3 (и.п.) 13 1971

XIII 2003

Тимошинин В.С., Годнев И.Н.,
Оптика и спектроскопия, 1971,
31, №6, 1027-1029 (русск.)

Постоянные кориолисова взаимодействия } галогенидов V группы. 20

Ф. хим. 1972, 8584 Ю

PF_3; AsF_3; SbF_3; BiF_3; BF_3; XIII 233

PCl_3; $AsCl_3$; $SbCl_3$; $BiCl_3$; BCl_3; 1972

PBr_3; $AsBr_3$; $SbBr_3$; $BiBr_3$; BBr_3; (пост. упро- бежн. растяж)

PI_3; AsI_3; SbI_3; BiI_3; BI_3

Тимошин В.С., Годиев И.Н.

Изв. высш. учеб. завед. физ., 1972, 15, N12, 141-3 (русск).

$ClOF_3$; POF_3; SO_2F_2; PCl_3; PBr_3; PF_3; PI_3; NH_3; PH_3; AsH_3; SbH_3 (XI 3790 структура) 1973

Hargittai I., Mijlhoff F.C.,

Chem. Weekbl., 1973, 69, N27, 9-10 (Neth.)

Prediction of molecular structure.

9

10 ⊕ CA, 1973, 79, N22, 129450g

paper rec. cmp, cal. n. (PF_3, PCl_3, PBr_3
XIII - 3936 (P_2I_3) 1975
Ewig C.S., Caffey P., Van Wazer J.R.,
Inorg. Chem, 1975, 14, n8, 1848-1857 (eng)
Use of pseudopotential theory to
study molecular structure. The
phosphorus halides. M-10361
Rel Zhur, 1976, 5647
10 6

РЖ3 опыл 4468 1975.

РЖ4 Kulkarni K.S, et al.

Indian J Pure and Appl.
Phys 1975. 13,
N11, 780-2.

(расчёт
эл. связи)

(сл С-3) III

РУ$_3$ Mohan S., 1976

Thirugnanasambandam P.

"Acta Cienc. Indica",
1976, 2(4), 359÷65.

(см. пост.)

III

(см. Ру$_3$)

PJ3

*C3-13546

1976

Murrell J.N., et al.

J. Chem. Soc. Dalton Trans., 1976, N9, 818-22

(Re, J. called).

(Cell PF3.)

1977

PJ3

Mohan S

Acta phys. polon.,
1977, A52, 747-51

(сек. PF3, III)

$PУ_3$ оттиск 5792 1977

таблица

ϑ_1

Shimanouchi T.

J. Phys. Chem. Ref. Data. 1977. 6. 993–1102.

Р У₃   Оттиск 8504   1979

Scharfenberg P.

молек. структ., кв. мех. расчёт

Chem. Phys. Lett., 1979, 65 (2), 304-309

(см. молек. структ.; VI)

РУ$_3$ 1980

Хамитов Ф.Г.

-взаимосв. геометрии и потенц. популяции

Докл. АН СССР 1980, 254, N4, 934-8.

см. NF3-III

PJ3

1981

Harcourt R. D.

Speculations Sci.

структура

Technol. 1981, 4(4),
367-374.

(see. N4, P4; III)

pg Ommick 12915 1981

Do, Ramani K., Khodgaonkar A.M.,

J. Chem. Educ., 1981, 58 (8), 609 – 610

РЖ 3

(Оп 2037) 1984

Grodzicki W., Walther H.,
Elbel Susanne.

Фотоэлектр. спектрст, структ., ч, диполь н. момент.

Z. Naturforsch., 1984, B39, N10, 1319–1330.

(см. NH3; III)

Xin M., Chow Chiu L., et al.

Фотоэлектр. спектр, расчет

J. Electron Spectrosc. and Relat. Phenom., 1984, 33, N2, 93–105.

РЖ | от. 36909 | 1992

геометрия,
колебат.
частоты,
ИК интенс.;
сил. поле,
ab initio
расчет.

Breidung J., Thiel W.,

J. Comput. Chem.,
1992, 13, N 2, 165–176.

РЖ3 (ОМ 36871) 1992

Блеев Ю.Г.,

Ж. орг. химии, 1992,
т. 66, N 12, с. 3258 - 3263.

(Сокр. PF_3; III)

PJ3

1993

Singh Prem,
Dublish A. K.
Indian J. Pure and
Appl. Phys. 1993. 31, N3. C.
193-194.

a.r. n.

(cog. BF3; III)

F: PI3
P: 3

1999

132:16588 Symmetry-broken inversion structures for Group 15 EX3 halides. Schwerdtfeger, Peter; Hunt, Patricia Department of Chemistry, The University of Auckland Auckland, N. Z. Adv. Mol. Struct. Res., 5, 223-262 (English) 1999 A review with 79 refs. The inversion process of EX3 Group 15 hydrides and halides is reviewed. All Group 15 hydrides EH3 and N halides NX3 inv through the classical D3h trigonal planar transition state. For the heav halides, however, the a2 HOMO can interchange with the a1 LUMO as pointed in 1980 by Marynick. Consequently, a low lying 1E' excited state can cou with the 1A1' ground state to undergo

C.A. 2000, 132

an e' 2nd-order Jahn-Teller (SOJT) distortion to a lower lying C2v inversion transition state. Hence, for t heavier Group 15 halides the Dixon-Arduengo edge inversion process throug T-shaped transition state is preferred. The potential energy surface (PE for these compds. is analyzed. For PF3, AsF3, SbF3, and BiF3 at the Hart Fock level the symmetry breaking occurs immediately upon distortion from C3v min. towards the D3h point of the PES. Different topologies around t sym. D3h point are possible in the planar EX3 arrangement, which connect T- and Y-shaped C2v structures. If e'-SOJT symmetry breaking occurs, the topologies can be derived from either a Mexican hat or a monkey saddle. the high-energy D3h point often cannot be described in a satisfactorily w by single-ref. methods. CASSCF calcns. show significant mixts. between 2 configurations of 1A1' symmetry, 1 which is described by a22a1'0 and deno as D3h(a2) and the 2nd configuration by a20a1'2 and denoted as D3h(a1'). Electron correlation effects are therefore important for the accurate det of the inversion barrier. For mols. with large configuration mixing (PCl PBr3, and PI3) a definite decision on the symmetry of the inversion struc cannot be made without higher level calcns. For the Bi halides the e'-SO distortion is small despite the energetically more favored D3h(a1') configuration. For these mols. the PES connecting the planar structures very shallow and a definite decision on the symmetry of the inversion transition state cannot be made. The question whether or not a mol. deco before it inverts is addressed. Common models for the inversion mechanis and bonding for the EX3 compds. are critically analyzed. Structures, vibrational

F: PI3
P: 3

2001

134:372013 **Density Functional Studies on the Lone Pair Effect of the Trivalent Group (V) Elements: I. Electronic Structure, Vibronic Coupling, and Chemical Criteria for the Occurrence of Lone Pair Distortions in AX3 Molecules (A=N to Bi; X=H, and F to I).** Atanasov, M.; Reinen, D. Fachbereich Chemie, Philipps-Universitaet und Zentrum fuer Materialwissenschaften, Marburg, Germany. J. Phys. Chem. A (2001), 105(22), 5450-5467. in English.

The energetic, steric, and bonding properties of mols. AX3 (A = N to Bi; X = H, F to I) are analyzed using d. functional theory. It is found that the "lone pair" in the initial D3h geometry is of central atom pz character for the NX3 and AH3 mols., whereas it possesses s symmetry in all other cases - here generally with a strong delocalization toward the ligands. The stabilization of the distorted C3v geometry is due mainly

to covalency effects, whereas steric interaction forces according to the Gillespie-Nyholm model do not seem to play a significant role. The application of the conventional vibronic pseudo Jahn-Teller coupling approach (PJT), here for the D3h→C3v transition [A1'⊗(α2" + α1')⊗A2" interaction], is an appropriate means for inorg. chemists to predict trends for the extent of distortion and for the corresponding energy gain. The vibronic coupling consts. and the vibronic stabilization energies, which mainly det. the total D3h→C3v energy gain, vary according to the sequences F > H > Cl > Br > I (A: N to Bi), and N > P > As > Sb > Bi (X: H,F), the dependence on A being only small or not present (X:Cl to I). Thus, the hardest mols. are the most susceptible to vibronic coupling, the latter energy being approx. imaged by the hardness difference η(C3v) - η(D3h). A roughly inverse trend is obsd. if the extent of the angular distortion τα from D3h to C3v symmetry is considered; here, the softest mols. such as Sb(Bi)Br3 exhibit the largest and NH3 the smallest deviations from D3h geometry. The different sequences for τα are due to the strong influence of the force const., which represents the C3v→D3h restoring energy. It is remarkable that the vibronic coupling energy is strongly correlated with the chem. hardness η (an observable quantity), while the stabilization energy for the D3h→C3v transition is not directly reflected by η, in contrast to what is generally called the "principle of max. hardness".