

## Polyazoaromatics

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After reading a review of azobenzenes, I noticed that all the examples were based on benzene and naphthalene mono or di-azo derivatives and not polyazoaromatics.

Wang, X. (2016). *Azo Polymers: Synthesis, Functions and Applications*. Springer. (Be careful if you work with these types of compounds as some are very toxic especially the aromatic hydrocarbons.) Searching for polyazoaromatics, I found the following reference:

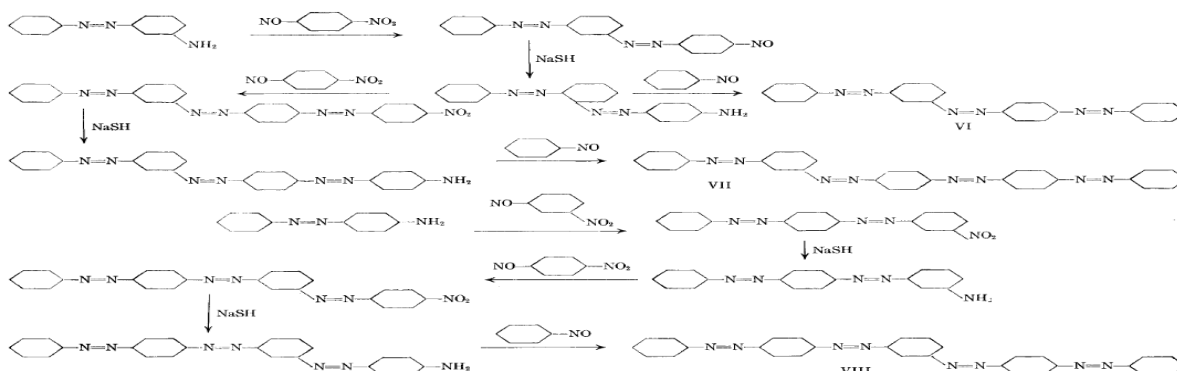


TABLE I: ULTRAVIOLET ABSORPTION OF POLYAZOBENZENES

I	Material	Chromatograph		Sample <sup>b</sup>	M.p., °C.	Color	Absorption			
		Sol-vent <sup>a</sup>	De-velop.				First band $\lambda_{max}$ $m\mu$	Second band $\lambda_{max}$ $m\mu$		
I	Azobenzene	P	P	E	67.5-68.0	Orange	319	20.5	440	0.5
II	4-Phenylazoazobenzene	P-B (1:1)	P-B (1:1)	E	168.5-169.0	Yellow-red	363	39.5	...	...
III	4,4'-Bis-(phenylazo)-azobenzene	B-C (1:1)	B-C (1:1)	E	236-236.5	Dark red	388	60.2	...	...
IV	3-Phenylazoazobenzene	B	B	E	80-80.5	Orange	325	41.4	446	1.0
V	3,3'-Bis-(phenylazo)-azobenzene	B-C (1:1)	B-C (1:1)	E	163.5-164.0	Yellow-brown	325	60.7	448	1.9
VI	3,4'-Bis-(phenylazo)-azobenzene	P	P	B	166-166.5	Orange-yellow	362	43.0	...	...
VII	3-Phenylazo-1'-( <i>p</i> -phenylazo)-phenylazoazobenzene	B-C (1:1)	B-C (1:1)	B	213.0-214.0	Brown-red	390	66.0	...	...
VIII	1,3-Bis-( <i>p</i> -phenylazophenylazo)-benzene	B-C (1:1)	B-C (1:1)	B	169.0-169.5	Dark red	370	50.0	...	...
IX	1,2-Bis-( <i>p</i> -phenylazo)-benzene	P-B (1:1)	P-B (1:1)	E	106.5-107.0	Red	305	35.0	...	...

<sup>a</sup> P, petroleum ether; B, benzene; C, chloroform. <sup>b</sup> E, sample was prepared from the effluent; B, sample was prepared by elution of an adsorbed band.

The features of the ultraviolet spectra of *p*-polyazobenzenes are given in Table I. A regular bathochromic shift as well as a regular increase of the extinction coefficient occurs as the number of *p*-phenylazo groups increases, similar to the behavior

of other linear-conjugated systems. The absorption curve of *trans*-azobenzene has two absorption bands in the ultraviolet region,<sup>4</sup> a strong band at 319  $m\mu$  (K band) and a weak band at 470  $m\mu$  (R band). The former is believed to be due to conjugation between the azo group and the benzene nucleus, the latter to the azo group alone. On increasing the number of azo groups, the weak R band is overcome by the strong absorption of the more powerful chromophore which is thought of as a resonance hybrid involving the entire molecule. This results in the formation of a single, strong absorption band for the higher homologs of the *p*-polyazobenzene series.

In case of *m*-polyazobenzenes one observes no shift of the wave length of the absorption maxima, but only a regular increase of the maximum extinction coefficient as the number of *m*-phenylazo groups goes up. As in the case of the *p*-polyazobenzenes, the extinction coefficient increases linearly with the number of azo groups; also the weak band at 470  $m\mu$  shows a regular increase which, however, is not observed in the para-series. In the case of *m*-polyazobenzenes no resonance structures involving the whole molecule can be written, and each azo group can be in conjugation only with the two benzene nuclei adjacent to it. Thus the absorption curves of *m*-polyazobenzenes can be represented by arithmetical addition of the contributions of each azobenzene system, and no shift of the  $\lambda_{max}$ -value occurs.

In the case of mixed *p*- and *m*-polyazobenzenes (VI, VII and VIII), the wave length at maximum absorption is determined by the number of azo groups in para position, and is almost the same as that of a *p*-polyazobenzene having the same number of azo groups. The intensity of absorption is related to, and roughly proportional to, the total number of azo groups in the molecule. These results are qualitatively explained by the resonance theory according to which only *p*-linked azo groups, as stated before, contribute to the length of the chromophoric system.

The absorption of 1,2-bis-(phenylazo)-benzene is quite different from the other compounds, exhibiting a hypsochromic effect. Since this is the only example observed in the *o*-series, we do not wish to offer any interpretation of the phenomenon until more data have been obtained.

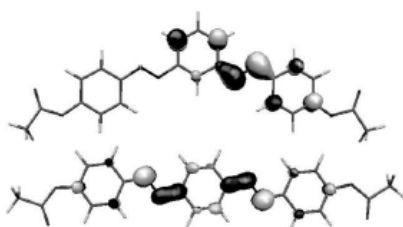
The above are from:

Ueno, K. (1952). Synthesis and Ultraviolet Absorption Spectra of Polyazobenzenes. *Journal of the American Chemical Society*, 74(18), 4508-4511.

Bellotto, S., Reuter, R., Heinis, C., & Wegner, H. A. (2011). Synthesis and Photochemical Properties of Oligo-ortho-azobenzenes. *The Journal of organic chemistry*, 76(23), 9826-9834. Apparently the ortho is like the para theoretically.

The main take away is the idea that para substituted polyazobenzenes are claimed to be conjugated and conductive while meta versions are not conjugated and not conductive.

**Alike yet different:** Two bis(azo) derivatives that can be viewed as a pair of azobenzene units sharing one of their phenyl rings and positioned either in *meta* or *para* positions relative to each other, exhibit markedly different photoisomerisation properties. Preferentially localised (*meta*) or delocalised (*para*)



electronic structures (see for instance the LUMO orbitals shown in the illustration) are responsible for the observed behaviour. These results are relevant for the design of novel photoelastic oligomers and polymers.

F. Cisnetti, R. Ballardini, A. Credi,\*  
M. T. Gandolfi, S. Masiero, F. Negri,\*  
S. Pieraccini, G. P. Spada . . . . 2011–2021

Photochemical and Electronic Properties  
of Conjugated Bis(azo) Compounds: An  
Experimental and Computational Study

**2004–10/8**

### Conclusion

The UV-visible absorption spectra, the *E*→*Z* photoisomerisation reaction and the electrochemical properties of two bis(azo) derivatives, (*E,E*)-*m*-1 and (*E,E*)-*p*-1, have been investigated. These two compounds are composed of a pair of azobenzene units sharing one of their phenyl rings, and differ only for the relative position of the two azo groups on the central phenyl ring. In summary, the absorption spectra

and photoisomerisation properties of (*E,E*)-*m*-1 are similar to those of (*E*)-azobenzene, while (*E,E*)-*p*-1 exhibits a substantial red shift in the absorption bands and a much decreased photoreactivity. From a detailed study on the quan-

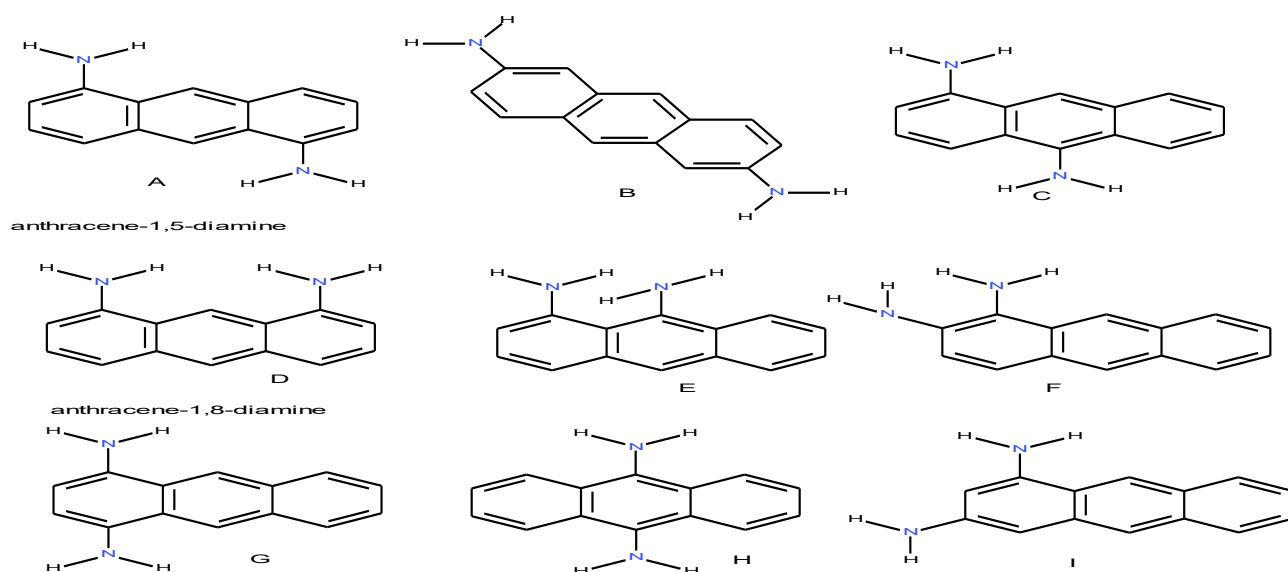
This reference confirms Ueno's above observation about meta vs para azo benzenes. So if you want a polyazoaromatic cis/trans active azo oligomer or polymer, it should be a meta benzene or contain such derivatives in the chain.

Reuter, R., & Wegner, H. A. (2012). meta-Oligoazobiphenyls—synthesis via site-selective Mills reaction and photochemical properties. *Beilstein journal of organic chemistry*, 8(1), 877-883.

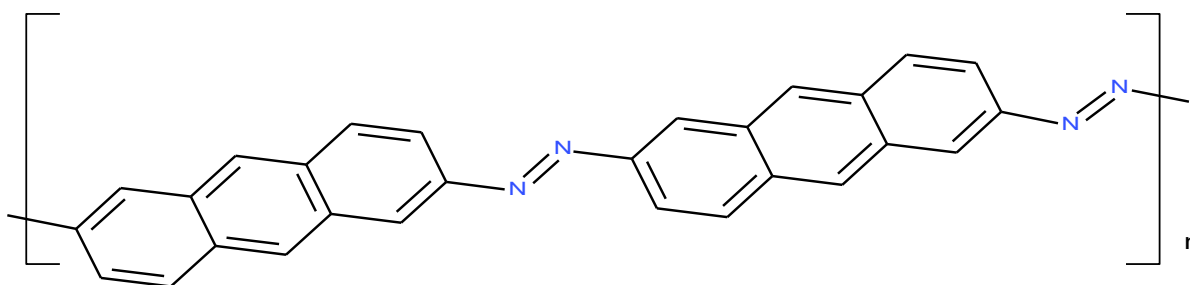
Vapaavuori, J., Goulet-Hanssens, A., Heikkinen, I. T., Barrett, C. J., & Priimagi, A. (2014). Are two azo groups better than one? Investigating the photo response of polymer-bisazobenzene complexes. *Chemistry of Materials*, 26(17), 5089-5096.

The problem is where to attach the azo groups in polyaromatics such as anthracene etc.

For example azo precursors:

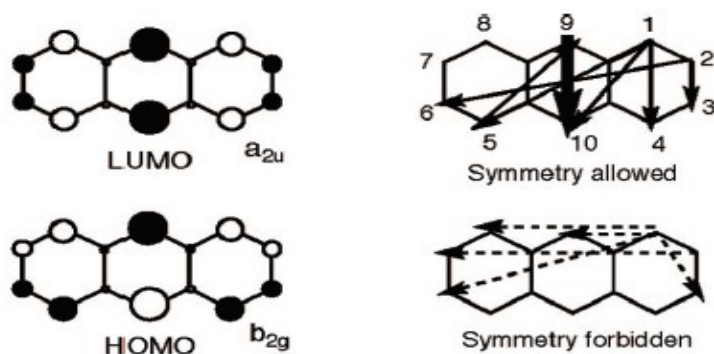


Scheme 1: I show amines but I would also use nitro derivatives as precursors. I would think that the most likely to be like the reference para polyazobenzenes examples, when converted to azo's, would be G followed by H or they could be equal. I show A&B because they too could be like the para polyazobenzenes. I is analogous to the meta examples. Now with more complicated aromatics you have more even more choices.

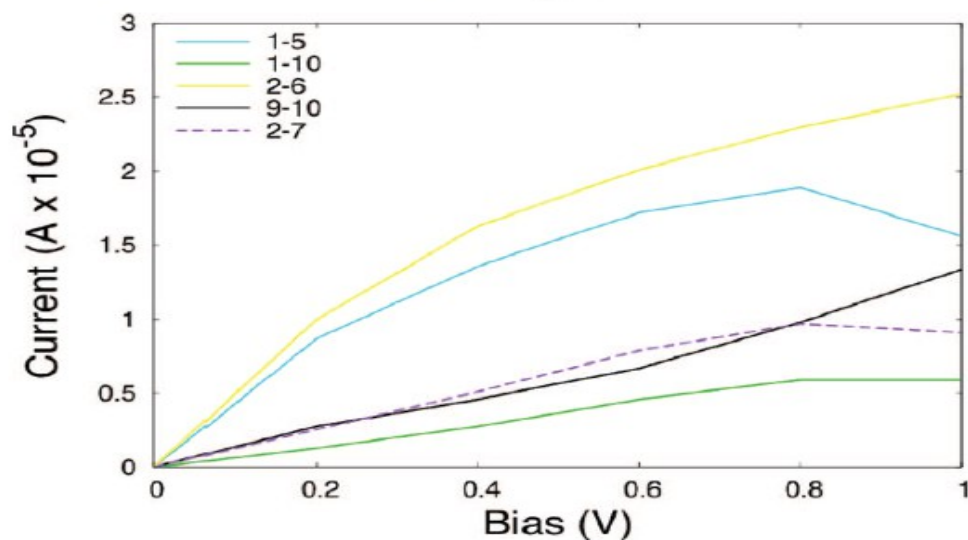


Scheme 2: (See scheme 4 for related synthesis) This position can result in a more linear polymer, but is this related to the meta or para positions in the polyazobenzenes? Additionally which is the best for cis/trans azo isomerism? I think the answer is to find

the actual electron flow at each anthracene position.



Referring to my scheme 1, this suggests that D,E,F and I are symmetry forbidden and not conductive pathways so they are analogous to the meta azobenzenes.



**Figure 9.** Computed transmission spectra and  $I-V$  curves for anthracene dithiolate junctions at the Perdew–Zunger LDA level of theory.

Yoshizawa, K., Tada, T., & Staykov, A. (2008). Orbital views of the electron transport in molecular devices. *Journal of the American Chemical Society*, 130(29), 9406-9413.

Yoshizawa, K. (2012). An orbital rule for electron transport in molecules. *Accounts of chemical research*, 45(9), 1612-1621.

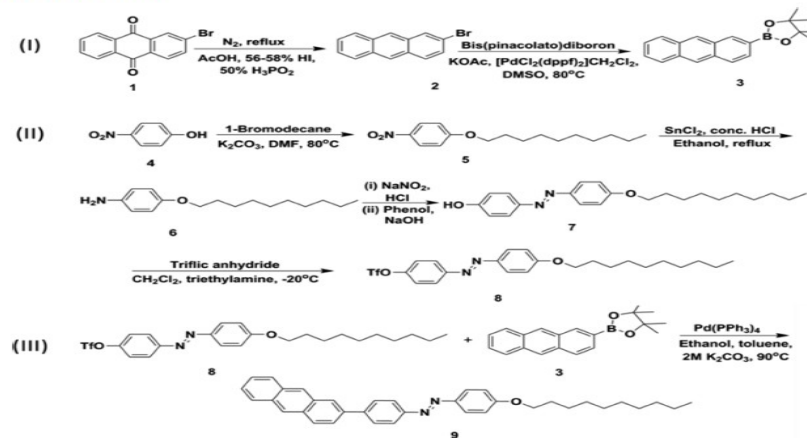
These papers are about the ability of the connections to anthracene (and other aromatics) to conduct charge. It seems that the first chart above shows the 9-10 connection being the most favored but the graph indicates that 2-6 connection is most conductive. This would suggest that my scheme 2 would be conductive hence conjugated throughout the azo linkage. The allowed positions are conductive, like the para substituted azobenzenes. The symmetry forbidden are like the meta azobenzenes.

Stuyver, T., Fias, S., De Proft, F., & Geerlings, P. (2015). Back of the envelope selection rule for molecular transmission: A curly arrow approach. *The Journal of Physical Chemistry C*, 119(47), 26390-26400.

Tsuji, Y., Estrada, E., Movassagh, R., & Hoffmann, R. (2018). Quantum interference, graphs, walks, and polynomials. *Chemical reviews*, 118(10), 4887-4911.

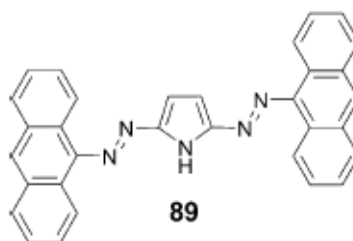
I have searched Google scholar extensively and found several pertinent references to azopolyaromatics employing anthracene or other polyaromatics. The synthesis of the anthracene isomers seem readily accomplished.

Scheme 1. Synthetic Routes of APDPD



Chen, Y., Li, C., Xu, X., Liu, M., He, Y., Murtaza, I., ... & Meng, H. (2017). Thermal and optical modulation of the carrier mobility in OTFTs based on an azo-anthracene liquid crystal organic semiconductor. *ACS Applied Materials & Interfaces*, 9(8), 7305-7314.

Although not what I had in mind, this is an interesting idea. Note that isomeration works here because this is a mono-azo derivative.

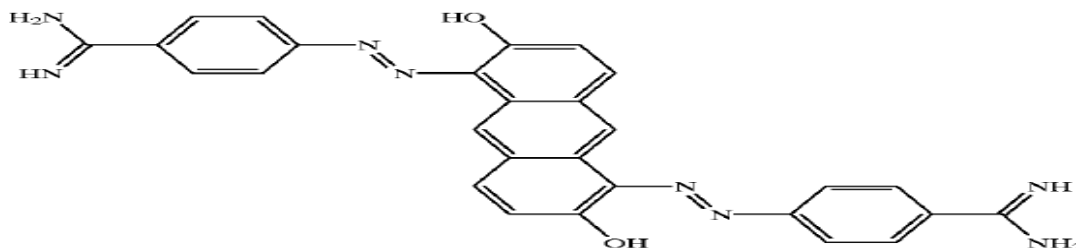


Mikroyannidis, J. A., Tsagkournos, D. V., Sharma, S. S., Kumar, A., Vijay, Y. K., & Sharma, G. D. (2010). Efficient bulk heterojunction solar cells based on low band gap bisazo dyes containing anthracene and/or pyrrole units.

*Solar energy materials and solar cells*, 94(12), 2318-2327.

Mishra, A., & Bäuerle, P. (2012). Small molecule organic semiconductors on the move: promises for future solar energy technology. *Angewandte Chemie International Edition*, 51(9), 2020-2067.

Dyes for solar cells in the literature show many examples of larger aromatics such as azo naphthalenes and anthracene but nothing larger?



(12) **United States Patent**  
**Lin et al.**

(10) **Patent No.:** **US 6,677,377 B2**  
(45) **Date of Patent:** **Jan. 13, 2004**

(54) **STRUCTURE BASED DISCOVERY OF INHIBITORS OF MATRIPTASE FOR THE TREATMENT OF CANCER AND OTHER CONDITIONS**

(75) Inventors: **Chen-Yong Lin**, Falls Church, VA (US); **Robert B. Dickson**, Kensington, MD (US); **Shaomeng Wang**, Rockville, MD (US); **Istvan Enyedy**, Hamden, CT (US); **Sheau-Ling Lee**, Falls Church, VA (US)

(73) Assignee: **Georgetown University School of Medicine**. Washington. DC (US)

(56) **References Cited**

**U.S. PATENT DOCUMENTS**

4,933,347 A \* 6/1990 Tidwell et al. .... 514/256  
4,963,589 A \* 10/1990 Tidwell et al. .... 514/636  
5,162,361 A \* 11/1992 Rosenthal et al. .... 514/396  
6,046,226 A \* 4/2000 Dykstra et al. .... 514/394

**OTHER PUBLICATIONS**

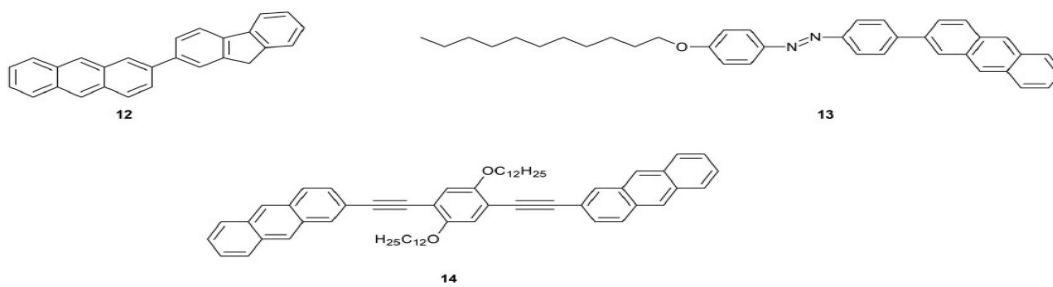
Bailly et al, *Biochem. J.* vol. 323, pp. 23–31 (1997).\*  
Enyedy et al, *J. Med. Chem.*, vol. 44, pp. 1349–1355 (2001).\*

The above examples are not related to my proposal, but polyazoacenes might be of great value. Unfortunately, no information concerning the above synthesis was disclosed.

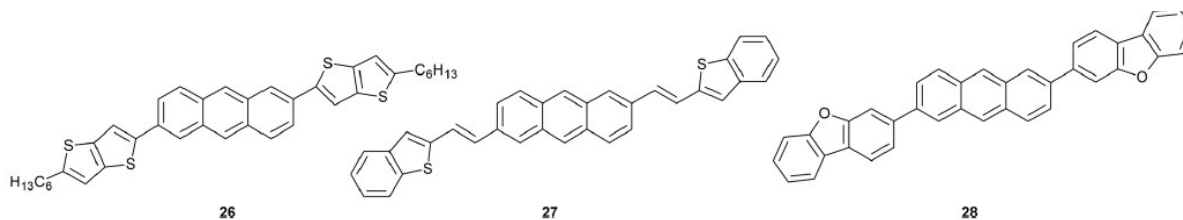
For more examples:

Merino, E. (2011). Synthesis of azobenzenes: the colored pieces of molecular materials. *Chemical Society Reviews*, 40(7), 3835-3853.

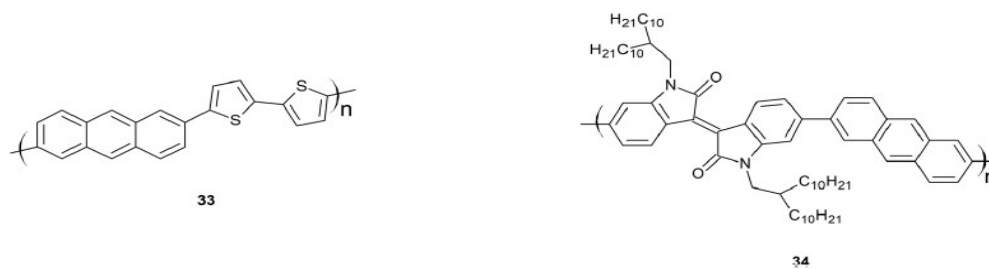
There many references to anthracene based compounds of significant interest for organic electronic applications. For example:



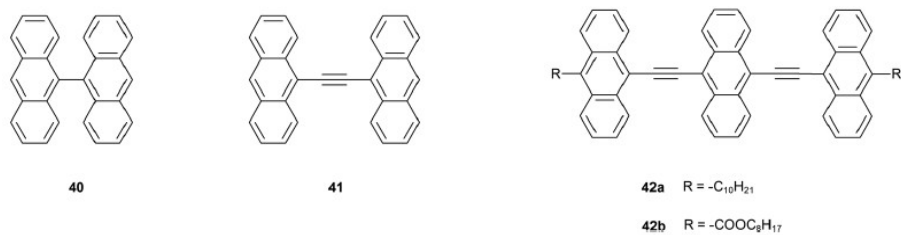
Scheme 3 Chemical structures of 2-substituted anthracene derivatives.



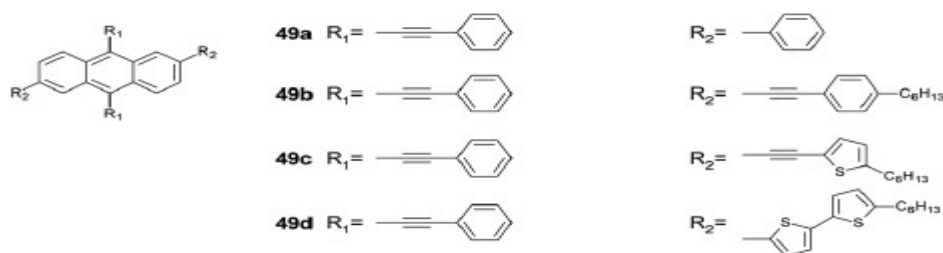
Scheme 4 Chemical structures of 2,6-substituted anthracene derivatives.



Scheme 5 Chemical structures of 2,6-substituted anthracene derivatives.



Scheme 6 Chemical structures of 9,10-substituted anthracene derivatives.

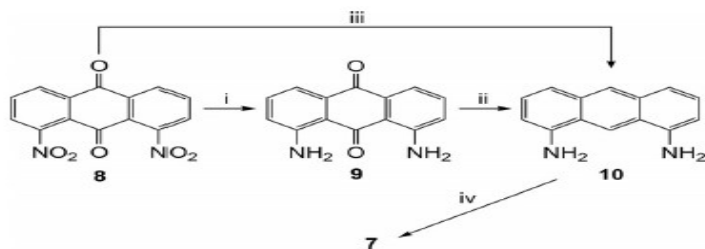


**Scheme 8** Chemical structures of 2,6,9,10-substituted anthracene derivatives.

“Furthermore, chemical modifications of anthracene would tune the molecular packing and charge transport properties, and fortunately, aryl groups, used to extend the p-system, like phenyl, naphthyl, and thienyl, could be very easily attached to anthracene at the active end- and peri-positions by coupling, including Suzuki coupling, Stille coupling, Negishi coupling, and Sonogashira coupling, in high yield, with an”

Chen, M., Yan, L., Zhao, Y., Murtaza, I., Meng, H., & Huang, W. (2018). Anthracene-based semiconductors for organic field-effect transistors. *Journal of Materials Chemistry C*, 6(28), 7416-7444.

The above are a small selection of the structures covered in this excellent review. This gives you an idea of the interest in anthracene derivatives. Also notice that all the positions are symmetry allowed affording conduction, in most cases, across the entire compound.



**Scheme 1.** Synthesis of anthracene bis(thio)ureas: (i)  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ,  $\text{EtOH}/\text{H}_2\text{O}$ , reflux, 65 h, 98%; (ii)  $\text{NaBH}_4$ ,  $\text{NaOH}$ , *i*PrOH, reflux, 16 h, 60%; (iii)  $\text{NaBH}_4$ , *i*PrOH, reflux, 43 h, 31%; (iv) 7O(P/N/F/F2):  $\text{ArNCO}$ ,  $\text{CH}_2\text{Cl}_2$ , reflux, 4–16 h, 50–90%, 7SF2: 3,5-( $\text{CF}_3$ ) $_2\text{C}_6\text{H}_3\text{NCS}$ , pyridine, RT, 21 h, 61%.

Dias, C. M., Valkenier, H., & Davis, A. P. (2018). Anthracene bisureas as powerful and accessible anion carriers. *Chemistry—A European Journal*, 24(23), 6262-6268.

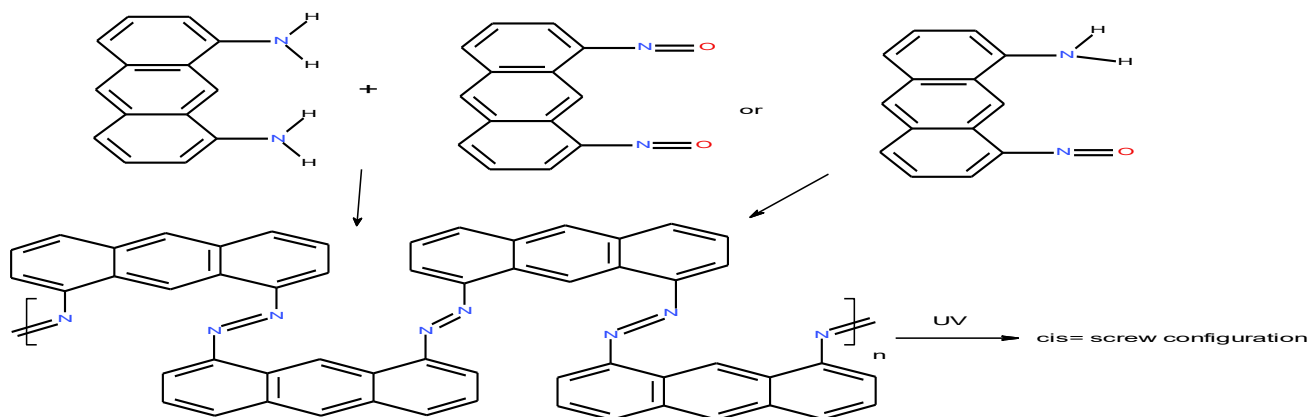
Converting this 1,8 diaminoanthracene to a diazo derivative should be possible. Let me refer you to a review of the following methods:

- (1) Azo coupling reaction
- (2) Mills reaction
- (3) Wallach reaction
- (4) Reduction of azoxybenzenes



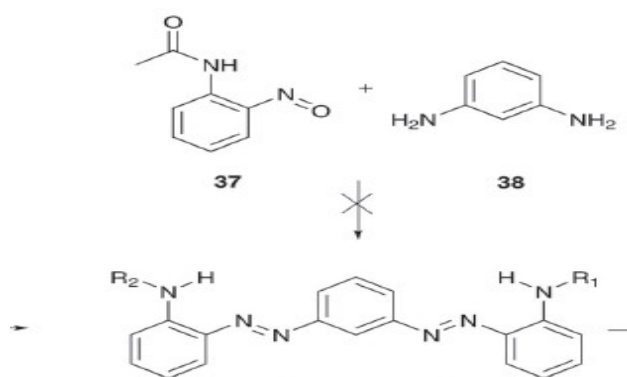
- (5) Reductive coupling of aromatic nitro derivatives
- (6) Oxidation of anilines
- (7) Dehydrogenation of arylhydrazines
- (8) Dimerization reaction of diazonium salts
- (9) Triazene rearrangement
- (10) Thermolysis of azides
- (11) Decomposition of N,N0-p-benzoquinonediimines dioxides
- (12) Reaction of arylcalcium derivatives with nitrous oxide
- (13) Metal catalyzed coupling of arylhydrazines
- (14) Opening of benzotriazoles
- (15) Reaction of quinones with arylhydrazines
- (16) Reaction of quinone acetals with arylhydrazines

Merino, E. (2011). Synthesis of azobenzenes: the coloured pieces of molecular materials. *Chemical Society Reviews*, 40(7), 3835-3853.



Scheme 4: Possible Mills reactions of 1,8 “forbidden symmetry” meta like polymer synthesis, capable of cis/trans isomerization? Also it is possible that along with the oligomer/polymer, a dimer can also form.

The above example is but one possibility of a forbidden symmetry derivative. Symmetry allowed versions can also be synthesized starting from dinitroanthracenes.



Tie, C., Gallucci, J. C., & Parquette, J. R. (2006). Helical conformational dynamics and photo isomerism of alternating pyridinedicarboxamide/m-(phenylazo) azobenzene oligomers. *Journal of the American Chemical Society*, 128(4), 1162-1171.

I point out the above reference because it might suggest a problem for my scheme 4; however, the problem here is that with the diamino benzene, the benzene is very electron rich and the reaction produces a mess based on reactions at both locations. This is not the case with the 1,8 diaminoanthracene because there is only one amine per aromatic ring.

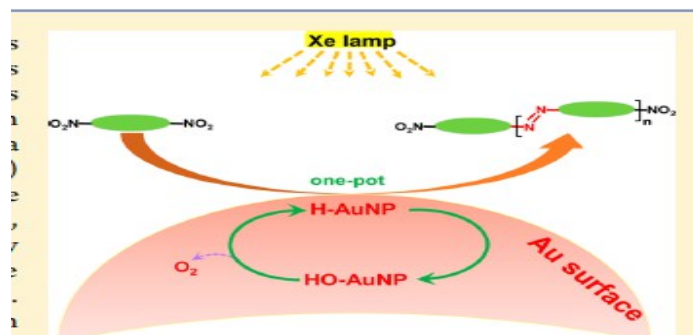
Synthesis:

“2,6-Dinitroanthracene was prepared by pyrolysis of a mixture of 2,6- and 2,7-dinitro-9,10-ethano-9,10- dihydroanthracene<sup>24</sup> and separated from the 2,7-dinitro isomer by a combination of column chromatography and fractional recrystallization from chlorobenzene, mp >300°; m/z 268 (M+); 1 H NMR (300 MHz; DMSO-d<sub>6</sub>) δ 9.28 (s, 2H<sub>1,4</sub>), 9.20 (s, 2H<sub>9,10</sub>), 8.42 (d, 2H<sub>3,6</sub> J ) 9.3 Hz), 8.42 (d, 2H<sub>4,8</sub> J ) 9.3 Hz). 4,4'-”

Tanida, H.; Ishitobi, H. *Tetrahedron Lett.* 1964, 15, 807 See the following reference:

Nelsen, S. F., Konradsson, A. E., Weaver, M. N., & Telo, J. P. (2003). Intervalence near-IR spectra of delocalized dinitroaromatic radical anions. *Journal of the American Chemical Society*, 125(41), 12493-12501.

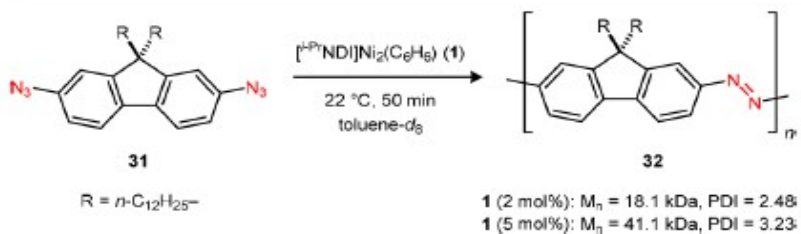
Currently there are recent references to new unique synthesis starting from nitro or azide derivatives.



This is very innovative!

Wang, L., Pan, X., Zhao, Y., Chen, Y., Zhang, W., Tu, Y., ... & Zhu, X. (2015). A straightforward protocol for the highly efficient preparation of main-chain azo polymers directly from bisnitroaromatic compounds by the photocatalytic process. *Macromolecules*, 48(5), 1289-1295.

Zhang, Y. F., & Mellah, M. (2017). Convenient electrocatalytic synthesis of azobenzenes from nitroaromatic derivatives using Sml<sub>2</sub>. *ACS Catalysis*, 7(12), 8480-8486.



**Figure 3.** Polymerization of **31** using catalyst **1**.

In order to examine the polymerization activity of catalyst **1**, we selected the diazide **31** as a model substrate (Figure 3). A related dinitrofluorene derivative was previously used to synthesize an azopolymer by a reductive method.<sup>24b</sup> Addition of **31** to solutions of **1** (2 or 5 mol %) in toluene- $d_8$  led to rapid monomer consumption and the formation of a deep red polymeric material (**32**), which was isolated in high yield by precipitation from MeOH (76% yield at 2 mol % loading of **1**). The molecular weight distribution of polymer **32** is sensitive to catalyst loading; for example, the average molecular weight is 18.1 kDa (PDI = 2.48) at 2 mol % but approximately doubles to 41.4 kDa (PDI = 3.23) at 5 mol %. This result highlights the potential for catalytic nitrene dimerization to be leveraged as a strategy to access tunable photoresponsive polymers containing main-chain azo bonds.

The above from this excellent work!!!!

Powers, I. G., Andjaba, J. M., Luo, X., Mei, J., & Uyeda, C. (2018). catalytic azoarene synthesis from aryl azides enabled by a dinuclear Ni complex. *Journal of the American Chemical Society*, 140(11), 4110-4118.

Thank you for reading this proposal.

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